Chemistry: Quantum Mechanics and Spectroscopy II

Tutorial Questions and Solutions

J. E. Parker
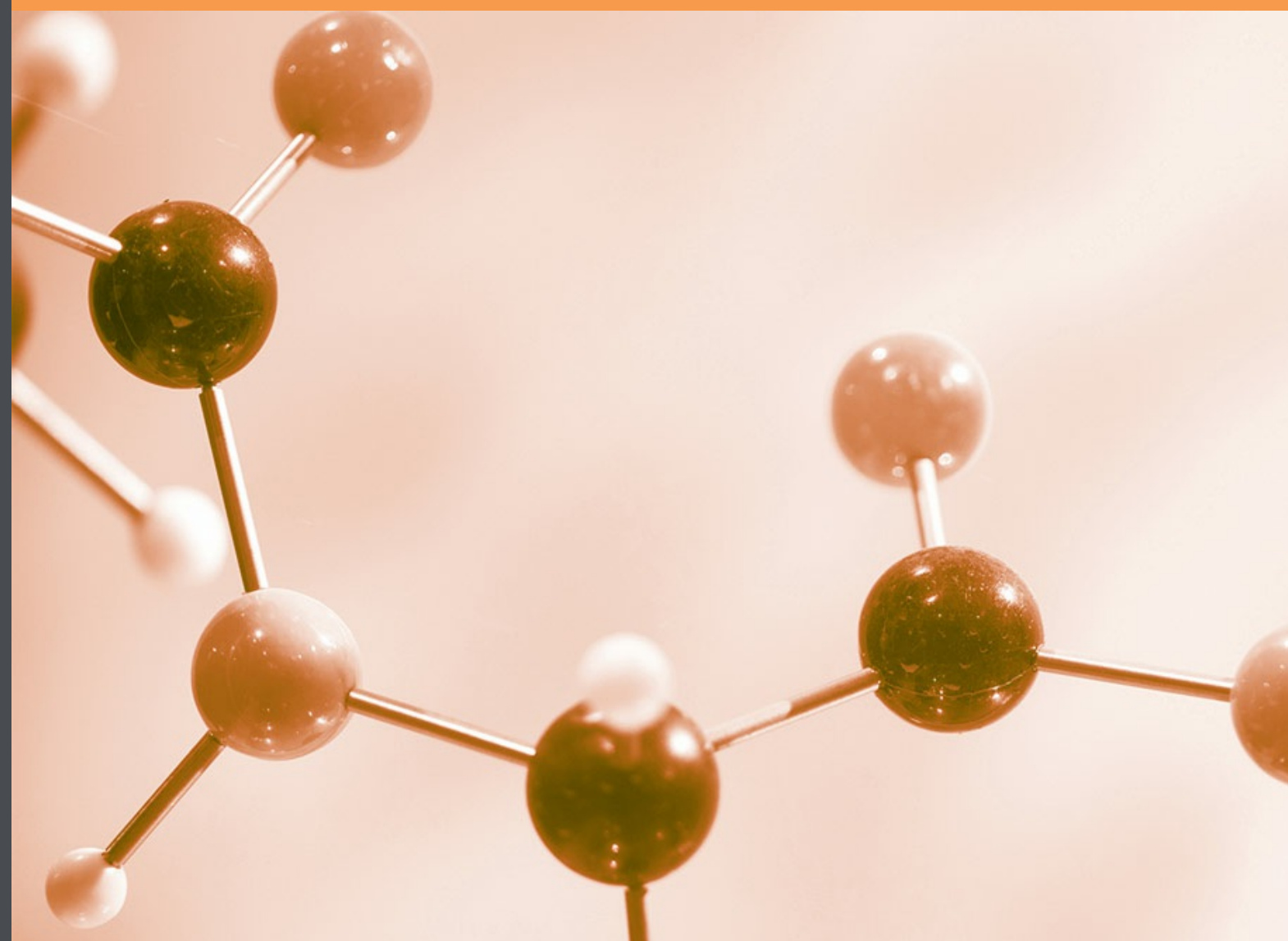
J.E. Parker

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Tutorial Questions and Solutions

Contents

Acknowledgements

This book is a collection of some of the questions and solutions I used in my first and second year quantum mechanics and spectroscopy lectures, workshops and tutorials at the Chemistry Department of Heriot-Watt University, Edinburgh Scotland. This book should be read in conjunction with the main test "Chemistry: Quantum Mechanics and Spectroscopy" (Parker 2015). Help with Maths and the carrying out of calculations may be found in Parker 2013b, 2012 and 2013a. To access these books see my web page below. Remember that workshop or tutorial questions will normally be longer and more complex than exam questions because you can use your textbooks, computer and fellow students so don't worry, they are not practice exam questions! This book and its companion textbook are designed to be used by Chemists, Physicists, Chemical Engineers, Biochemists and Biologists in a typical first and second year degree course. I wish you all good luck with your studies.

I would like to thank the staff and students at Heriot-Watt who over the years have helped to shape this book. However, my main thanks are to Jennifer for her patient and help during the writing of these books.

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1 Quantum Mechanics Tutorial

Look up any physical constants you require in your textbook. Work to an appropriate number of significant figures (typically 4–6) and use units throughout. Attempt each question before checking with the solution. When appropriate we will make use of the following units conversion to express the named unit for energy, joule, in the SI base units. The conversion comes from the definition of energy in terms of force (unit newton, symbol N) combined with the definition of energy (unit joule, symbol J).

$$\text{force} = \text{mass} \times \text{acceleration} \qquad 1\,\text{N} = \text{kg m s}^{-2}$$
$$\text{energy} = \text{force} \times \text{distance} \qquad 1\,\text{J} = 1\,\text{kg m}^2\,\text{s}^{-2}$$

1.1 Question

For each of the following photon energies find the frequency (in s^{-1} or Hz) and wavelength of the light. State to which part of the electromagnetic spectrum each photon belongs.

a) 2.185×10^{-22} J.

b) 6.554×10^{-20} J.

c) 3.547×10^{-19} J.
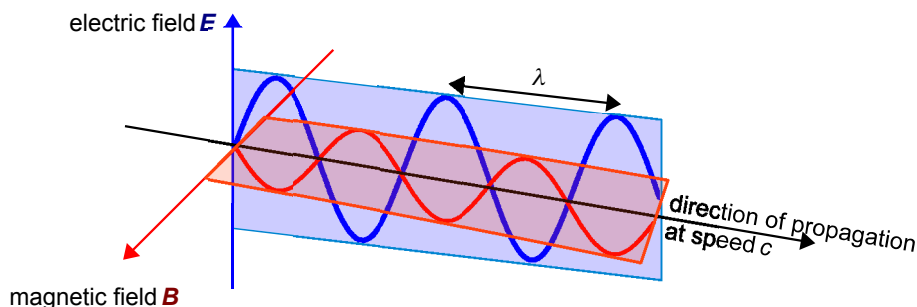
Figure 1.1: plane polarized light **E**, **B** and c are at mutual right angles.

1.2   Question

Microwave photons are not very energetic, however, this radiation cooks your food in the microwave oven. If you bombard a cherry pie with photons with a wavelength of 0.50 cm calculate the following.

a) The frequency of this radiation.
b) If you bombard the pie with 1.00 mole of photons (called an einstein), how much energy does your pie absorb?
c) If the cherry pie takes 8.368 J to heat 1 g of it by 1°C (its heat capacity) how many einsteins of 0.50 cm microwaves are required to heat a 150 g pie from 4°C (from the fridge) to 60 °C?

1.3   Question

One of the series in the H atom emission spectrum is the Pfund series. It is due to the quantum jumps from high levels down to $n = 5$. Calculate the wavelength and frequency of the lowest energy line in this series and describe what region of the electromagnetic spectrum it is in.

1.4   Question

Assume you are an engineer designing a space probe to land on a distant planet. You wish to use a photoelectric metal in your switch which requires 6.7×10^{-19} J atom^{-1} to remove an electron. You know the atmosphere of the planet filters out light less than 540 nm. Calculate the threshold frequency required to make the device work, and the corresponding wavelength of light required. Will the device work on the planet in question?
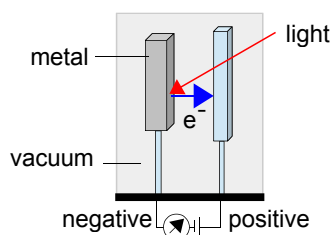

Figure 1.2: photoelectric switch.

1.5   Question

Calculate the de Broglie wavelength of the following particles.

   a) An electron travelling at 6.06×10^7 m s^{-1}.
   b) An O_2 molecule travelling at 500 m s^{-1}.
   c) A double-decker bus in Edinburgh (mass 16000 kg) travelling at 20 miles per hour (8.9 m s^{-1}).

1.6   Question

Heisenberg's uncertainty principle tells us that we cannot know the position and momentum of a particle simultaneously to arbitrary precision.

   a) For an electron in a 5 nm long box, what is the minimum uncertainty in the velocity?
   b) If we know the velocity of an O_2 molecule to a precision of 5 m s^{-1}, what is the minimum uncertainty in its position?
   c) If we know the velocity of a football (mass = 0.200 kg) to a precision of 5 m s^{-1}, what is the minimum uncertainty in its position?

1.7   Question

The particle in a 1-dimensional box is a reasonable model for an electron in a conjugated polyene (free electron molecular orbital model FEMO). Such a molecule is hexatriene $CH_2=CH-CH=CH-CH=CH_2$ which contains 3 double and 2 single bonds alternating along the chain.

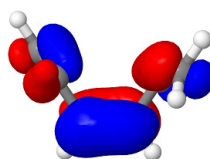**Figure 1.3:** hexatriene HOMO.

Assume that each CC bond in a conjugated diene can be taken as having an average length of 1.40 Å but think carefully about the total length available to the π-electrons.

   a) Calculate the energies of the first four levels in joules.
   b) What is the zero point energy of an electron in the molecule?

c) If each double bond contributes two electrons, what is the wavelength of a transition that excites an electron from the top-most filled level (HOMO) to the lowest empty level (LUMO)?
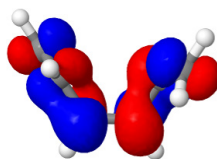
Figure 1.4: hexatriene LUMO.

1.8   Question

Give the quantum number associated with each of the following and the possible values they may take.

a) Orbital energy of the electron in the H atom.
b) Orbital shape.
c) Orbital size.
d) Orbital orientation.
e) How many subshells are there in the $n = 3$ shell and what are they?
f) How many orbitals are there in the f subshell and what are they?

1.9   Question

a) For an electron in an atomic orbital, explain what information is contained in the functions ψ, ψ^2 and $4\pi r^2 \psi^2$.
b) Sketch the shapes of ψ, ψ^2 and $4\pi r^2 \psi^2$ for the H-atom 1s and 2s orbitals. Mark the position of the Bohr radius a_0.
c) Explain carefully what is meant by a boundary surface for an atomic orbital. Sketch these surfaces for all possible orbitals with $n = 2$, including suitably labelled axes.

1.1   Solution

The energy of a single photon is $E = h\nu$ (ν is the frequency and h is Planck's constant $h = 6.626\times10^{-34}$ J s). The wavelength is related to the frequency by the speed of light in a vacuum, $c = 2.998\times10^8$ m s^{-1}. Hence the frequencies and wavelengths are calculated below.

$$E = h\nu \quad \nu = \frac{E}{h} \quad c = \lambda\nu \quad \lambda = \frac{c}{\nu}$$

$$(a)\ \nu = \frac{2.185\times10^{-22}\,\text{J}}{6.626\times10^{-34}\,\text{J s}} = 3.298\times10^{11}\,\text{s}^{-1} \quad \lambda = \frac{2.998\times10^8\,\text{m s}^{-1}}{3.298\times10^{11}\,\text{s}^{-1}} = 9.090\times10^{-4}\,\text{m} = 0.909\,\text{mm}$$

$$(b)\ \nu = \frac{6.554\times10^{-20}\,\text{J}}{6.626\times10^{-34}\,\text{J s}} = 9.891\times10^{13}\,\text{s}^{-1} \quad \lambda = \frac{2.998\times10^8\,\text{m s}^{-1}}{9.891\times10^{13}\,\text{s}^{-1}} = 3.031\times10^{-6}\,\text{m} = 3.031\,\mu\text{m}$$

$$(c)\ \nu = \frac{3.547\times10^{-19}\,\text{J}}{6.626\times10^{-34}\,\text{J s}} = 5.353\times10^{14}\,\text{s}^{-1} \quad \lambda = \frac{2.998\times10^8\,\text{m s}^{-1}}{5.353\times10^{14}\,\text{s}^{-1}} = 5.601\times10^{-7}\,\text{m} = 560.1\,\text{nm}$$

a) is in the microwave/infra-red "boundary", (b) infra-red and (c) visible (a yellow-green colour) regions of the electromagnetic spectrum.
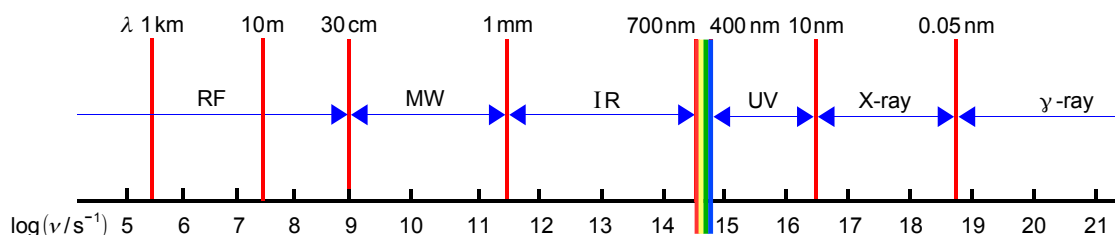

Figure 1.5: electromagnetic spectrum.

1.2   Solution

The MW radiation has $\lambda = 0.50$ cm $= 0.50\times10^{-2}$ m and the energy of an einstein varies with λ.

$$(a)\ c = \lambda\nu \quad \nu = c/\lambda = \frac{2.998\times10^8\,\text{m s}^{-1}}{0.50\times10^{-2}\,\text{m}} = 5.996\times10^{10}\,\text{s}^{-1}$$

$$(b)\ E = h\nu = \left(6.626\times10^{-34}\,\text{J s}\right)\left(5.996\times10^{10}\,\text{s}^{-1}\right) = 3.973\times10^{-23}\,\text{J}$$

$$E_{\text{einstein}} = N_A\times E = \left(6.022\times10^{23}\,\text{mol}^{-1}\right)\left(3.973\times10^{-23}\,\text{J}\right) = 23.93\,\text{J mol}^{-1}$$

$$(c)\ \Delta T = 60^\circ\text{C} - 4^\circ\text{C} = 56^\circ\text{C} = 56\,\text{K}$$

$$\text{energy required} = \left(8.368\,\text{J g}^{-1}\text{K}^{-1}\right)\left(150\,\text{g}\right)\left(56\,\text{K}\right) = 7.0291\times10^4\,\text{J}$$

$$\text{photons required} = \frac{7.0291\times10^4\,\text{J}}{23.93\,\text{J mol}^{-1}} = 2.937\times10^3\,\text{mol of photons}$$

1.3 Solution

$$\bar{v} = R_\text{H}\left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right)$$

$$\bar{v} = 1.09677{\times}10^5\,\text{cm}^{-1}\left(\frac{1}{5^2} - \frac{1}{6^2}\right) = 1.09677{\times}10^5\,\text{cm}^{-1}{\times}0.01222 = 1.3405{\times}10^3\,\text{cm}^{-1}$$

$$\bar{v} = \frac{1}{\lambda} \qquad \lambda = \frac{1}{1.3405{\times}10^3\,\text{cm}^{-1}} = 7.4599{\times}10^{-4}\,\text{cm} = 7.4599\,\mu\text{m}$$

Wavelength λ = 7.4599 μm is in the infrared. To find the frequency we rearrange $c = \lambda v$ to give $v = c/\lambda$.

$$v = \frac{\left(2.998{\times}10^8\,\text{m s}^{-1}\right)}{\left(7.4599{\times}10^{-6}\,\text{m}\right)} = 4.0188{\times}10^{13}\,\text{s}^{-1}$$

1.4 Solution

$$E = h\nu \quad \nu = \frac{E}{h} \quad \nu_{\text{threshold}} = \frac{(6.7 \times 10^{-19}\,\text{J})}{(6.626 \times 10^{-34}\,\text{J s})} = 1.011 \times 10^{15}\,\text{s}^{-1}$$

$$c = \lambda \nu \quad \lambda_{\text{threshold}} = \frac{c}{\nu_{\text{threshold}}} = \frac{(2.998 \times 10^{8}\,\text{m s}^{-1})}{(1.011 \times 10^{15}\,\text{s}^{-1})} = 2.965 \times 10^{-7}\,\text{m} = 296.5\,\text{nm}$$

The threshold wavelength (296.5 nm) a smaller than what the atmosphere will let through (cut off 540 nm). The design would not work and it would be an expensive mistake to rely on this design!

1.5 Solution

The de Broglie wave length is given by $\lambda = h/mv$, where m is the mass of the particle and v is its velocity. Remember that the SI unit of mass is the kilogram and not the gram.

$$(\text{a})\ \lambda = \frac{6.626 \times 10^{-34}\,\text{J s}}{(9.1094 \times 10^{-31}\,\text{kg})(6.06 \times 10^{7}\,\text{m s}^{-1})} = 1.200 \times 10^{-11}\,\text{m} = 12\,\text{pm}$$

$$(\text{b})\ \lambda = \frac{6.626 \times 10^{-34}\,\text{J s}}{(32 \times 1.6605 \times 10^{-27}\,\text{kg})(500\,\text{m s}^{-1})} = 2.494 \times 10^{-11}\,\text{m} = 24.94\,\text{pm}$$

$$(\text{c})\ \lambda = \frac{6.626 \times 10^{-34}\,\text{J s}}{(16000\,\text{kg})(8.9\,\text{m s}^{-1})} = 4.653 \times 10^{-39}\,\text{m}$$

The electron in (a) has a wavelength suitable for electron diffraction which is used to find molecular structures. The oxygen molecule (b) is moving at a typical average thermal velocity, indicating the typical de Broglie wavelength of a free gas phase molecule. The bus has a wavelength smaller than any possible physical measurement, illustrating why you don't find buses diffracting all over the place, although it sometimes seems that they do when driving in Edinburgh!

1.6   Solution

$$\Delta p\,\Delta x \geq \frac{h}{4\pi} \quad \text{using} \quad 1\text{ J} = 1\text{ kg m}^2\text{s}^{-2} \quad \text{also} \quad \Delta p = m\Delta v$$

$$(\text{a})\ \Delta p = \frac{h}{4\pi\Delta x} = \frac{6.626\times 10^{-34}\text{ J s}}{4\pi(5\times 10^{-9}\text{m})} = 1.055\times 10^{-26}\text{ kg m s}^{-1}$$

$$\Delta v = \frac{\Delta p}{m} = \frac{1.055\times 10^{-26}\text{ kg m s}^{-1}}{9.109\times 10^{-31}\text{ kg}} = 1.158\times 10^{4}\text{m s}^{-1}$$

$$(\text{b})\ \Delta x = \frac{h}{4\pi\Delta p} = \frac{h}{4\pi m\Delta v} = \frac{6.626\times 10^{-34}\text{ J s}}{4\pi(32\times 1.661\times 10^{-27}\text{kg})(5\text{ m s}^{-1})} = 1.984\times 10^{-10}\text{ m}$$

$$(\text{c})\ \Delta x = \frac{h}{4\pi\Delta p} = \frac{h}{4\pi m\Delta v} = \frac{6.626\times 10^{-34}\text{ J s}}{4\pi(0.200\text{ kg})(5\text{ m s}^{-1})} = 5.273\times 10^{-35}\text{m}$$

In (a) the electron has a large uncertainty in its velocity in its 5 nm size box. In (b) the uncertainty in the position is of the order of the size of the molecule. The uncertainty of the position of the football (c) is too small to be experimentally measurable, hence we don't have any difficulty in determining the velocity and position of the macroscopic objects we encounter in the everyday world.

1.7   Solution

a) Each bond is assumed to be 1.40 Å = 1.40×10⁻¹⁰ m long, and there are 5 bonds. Making the rough approximation that L is equal to the sum of the average lengths of the CC bonds, plus the π-electrons do not stop dead at the carbon nuclei of the terminal atoms but go out to the "radius" of each terminal C-atom. The electrons can travel beyond the nucleus of each of the terminal C-atoms by about half an average CC bond length at each end of the molecule gives us a box length of $L = 6\times 1.4\times 10^{-10}$ m. Assuming the FEMO model the energies of the π-electrons in a hexatriene molecule are given below.

$$E = \frac{n^2 h^2}{8\,m\,L^2} = \frac{n^2(6.626\times 10^{-34}\text{ J s})^2}{8(9.109\times 10^{-31}\text{ kg})(6\times 1.40\times 10^{-10}\text{ m})^2} = n^2\,8.5385\times 10^{-20}\text{J}$$

$$E(n{=}1) = 8.5385\times 10^{-20}\text{J}$$
$$E(n{=}2) = 3.4154\times 10^{-19}\text{J}$$
$$E(n{=}3) = 7.6847\times 10^{-19}\text{J}$$
$$E(n{=}4) = 1.3662\times 10^{-18}\text{J}$$

b) The zero point energy (ZPE) of the particle in the box is given by the energy of the lowest level, $n = 1$, and so the FEMO model gives the ZPE = 8.5385×10⁻²⁰ J.

c) Each π-bond contributes two electrons with a total of 6 π-electrons. From Pauli's exclusion principle you can fit two π-electrons into each energy level, equivalent to a π-orbital. So the excitation of an electron from the HOMO to the LUMO is the equivalent of exciting it from the level with $n = 3$ to the level with $n = 4$.

$$\Delta E(4 \leftarrow 3) = 1.3662 \times 10^{-18} \text{J} - 7.6847 \times 10^{-19} \text{J} = 5.9773 \times 10^{-19} \text{J}$$

$$E = h\nu \quad \nu = \frac{E}{h} = \frac{5.9773 \times 10^{-19} \text{J}}{6.626 \times 10^{-34} \text{J s}} = 9.0210 \times 10^{14} \text{s}^{-1}$$

$$c = \lambda\nu \quad \lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8} \text{m s}^{-1}}{9.0210 \times 10^{14} \text{s}^{-1}} = 332.3 \text{nm}$$

This FEMO approximate wavelength is crude when compared with experiment ($\lambda_{max} = 263$ nm). However, the FENMO model is a useful first approximation as it predicts that the electronic absorption spectra of small conjugated polyenes are in the UV region. Also as the length of the conjugated molecule increases it predicts that the absorption moves from the UV into the visible and then through the visible from the blue end to the red end.

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1.8   Solution

a) From the Bohr theory the orbital energy of the electron in the H-atom is $E = -R_\mathrm{H}/n^2$ where n is the principal quantum number $n = 1, 2, 3, \cdots$.

b) Orbital shape is determined by l the angular momentum quantum number, and $l = 0, 1, 2, 3, \cdots,$ $(n-1)$ but normally l is symbolized by the labels s, p, d, f.

c) Orbital size is determined by n the principal quantum number.

d) Orbital orientation is determined by m_l the component of the angular momentum quantum number along a chosen direction (also called the magnetic quantum number) $m_l = 0, \pm1, \pm2,$ $\pm3, \cdots, \pm l$.

e) For $n = 3$, the subshells are $l = 0, 1, 2$, or 3s, 3p, 3d. So there are three subshells.

f) The f subshell ($l = 3$) has 7 orbitals having $m_l = 0, \pm1, \pm2, \pm3$. The f orbitals are filled up through the inner-transition elements (lanthanoids and actinoids) in the periodic table.

1.9   Solution

a) The wavefunction ψ measures the probability amplitude and has both positive and negative regions just like any other wave, *e.g.* waves in water or waves on a piece of string. The allowed solutions have to meet the boundary conditions and are standing waves for time-independent solutions, *i.e.* for solutions which persist through time.

The function $|\psi|^2$ is called the probability density and is the square of the wavefunction or the square of the modulus, where $|\psi|^2 = \psi^*\psi$ if ψ is complex (Parker 2013a, p. 52, 69). The probability density $|\psi|^2$ can only have positive real values. For an electron in an atomic orbital ψ^2 describes the probability of finding the electron in a small volume ($d\tau$) at a certain distance r from the nucleus in any one particular direction. The probability density will vary with the direction for p, d, f atomic orbitals. The probability is the product of the small element of volume $d\tau$ and the probability density $|\psi|^2$.
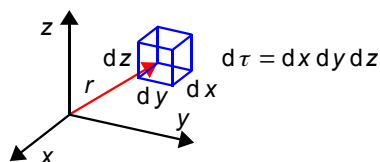

Figure 1.6: definition of the small volume at a distance r from the nucleus.

The function $4\pi r^2\psi^2$ is known as the radial distribution function. It describes the probability of finding the electron in a thin spherical *shell* a distance r from the nucleus in *all* possible directions rather like a thin layer of an onion.
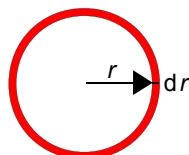

Figure 1.7: cross-section though an annular spherical shell around a nucleus.

The surface area of the inner sphere of radius r is $4\pi r^2$ and if the outer sphere is a small distance dr larger radius than the inner sphere then the volume of the spherical shell is $4\pi r^2 dr$. As dr is made infinitesimally small the radial distribution function within the spherical shell becomes $P(r) = 4\pi r^2\psi^2$.

 b) Reasonable hand drawn sketches are expected which should look similar to Figs. 1.8 and 1.9.
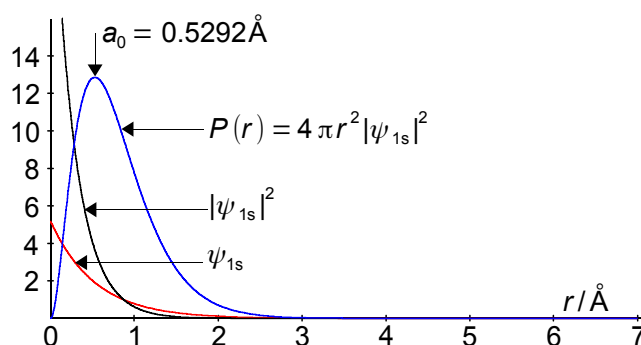

Figure 1.8: the H-atom 1s wavefunction, probability density and radial distribution function.

The radial distribution function $P(r)$ for the 1s AO consists of two terms, $4\pi r^2$ increases with r, but ψ^2 decreases with r and their product will have a maximum at the Bohr radius $a_0 = 0.5292$ Å.
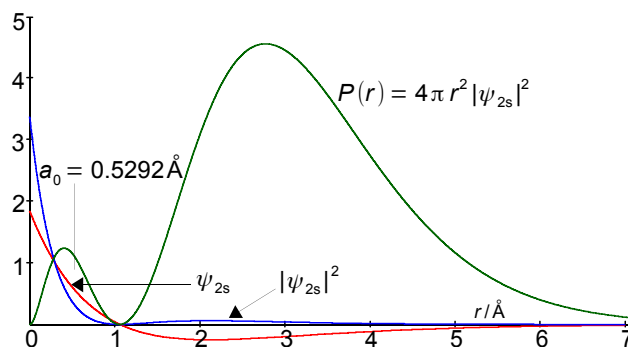

Figure 1.9: the H-atom 2s wavefunction, probability density and radial distribution function.

Note that the vertical axes of the two figures are different as the 2s atomic orbital is more spread out radially and has a lower peak intensity.

$$P(r) = 4\pi r^2 \psi_{1s}^2 = 4\pi r^2 \left(2 \left(\frac{Z}{a_0} \right)^{3/2} \exp\left(-\frac{Zr}{a_0} \right) \right)^2$$

$$P(r) = 4\pi r^2 \psi_{2s}^2 = 4\pi r^2 \left(\frac{1}{8^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) \exp\left(-\frac{Zr}{2a_0} \right) \right)^2$$

The $P(r)$ for the 2s AO consists of three terms; firstly $4\pi r^2$ increases with r, secondly $(2 - Zr/a_0)$ is positive and decreases with r until $r = 2a_0/Z$ when it is increasingly negative and thirdly the exponential term decreases with r. This the radial distribution function $P(r)$ for the 2s AO consists of two maxima with the outer one larger. Radial distribution functions can be measured experimentally using electron diffraction methods.

c) A boundary surface defines the region around the nucleus within which the electron will be found with a stated total probability, typically, 90%. The subshells for $n = 2$ are 2s and $2p_x$, $2p_y$ and $2p_z$ with the 2s orbital having a spherical boundary surface and the 2p orbitals having two lobes directed along each of the three Cartesian axes.
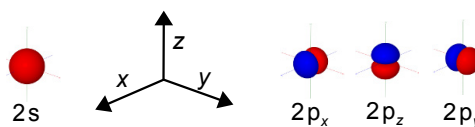
Figure 1.10: molecular orbitals.

2 Rotational Spectroscopy Tutorial

2.1 Question

Which of the following molecules have a pure rotational spectrum: (a) H_2, (b) HCl, (c) CH_4, (d) CH_2Cl_2, (e) $CHCl_3$, (f) H_2O, (g) H_2O_2 and (h) NH_3?

2.2 Question

The molecule $^{14}N^{16}O$ absorbs in the microwave region with a gap of 3.390 cm^{-1} between adjacent lines in the spectrum. Calculate (a) the rotational constant B, (b) the moment of inertia I, (c) the reduced mass μ, and (d) the average bond length of the molecule.

2.3 Question

Give the timescales and explain fully why the $^{14}N^{16}O$ bond length is referred to as an average bond length.

2.4 Question

For the $^{14}N^{16}O$ molecule estimate the ratio of the populations of the $J = 15$ to $J = 7$ levels at 298.15 K.

2.5 Question

If the $\Delta J = 2,3$ rotational transition for a diatomic molecule occurs at $\bar{v} = 2.00$ cm, find $\bar{v}$ for the $\Delta J = 8,7$ transition for this molecule.

2.6   Question

The rotational constants for the four most common isotopomers of hydrogen bromide (ignoring tritium) are listed below. Calculate the bond distance r_0 in each of these molecules neglecting centrifugal distortion and comment on your results.

	$^1\mathrm{H}\,^{79}\mathrm{Br}$	$^1\mathrm{H}\,^{81}\mathrm{Br}$	$^2\mathrm{H}\,^{79}\mathrm{Br}$	$^2\mathrm{H}\,^{81}\mathrm{Br}$
B_0/MHz	250357.599	250250.202	127357.6343	127279.7614

2.7   Question

The pure rotational spectrum of the isotopomer $^1\mathrm{H}^{127}\mathrm{I}$ consists of a series of approximately equally spaced lines with a separation between neighbouring lines of 13.10 cm^{-1}. Calculate the bond length of the molecule.

2.8   Question

The bond length of $^{14}N^{16}O$ is $r_0 = 1.15$ Å, calculate the wavenumber of the $\Delta J = 5,4$ assuming the molecule is a rigid rotor.

2.1   Solution

A molecule must have a *permanent* dipole moment and be in the *gas* phase to have a pure rotational spectrum. (a) H_2 is MW inactive, (b) HCl gas is active but hydrochloric acid solution is inactive, (c) CH_4 is inactive, (d) for CH_2Cl_2 the cis isomer 1,1-dichloroethene is active but the trans isomer 1,2-dichloroethene inactive,
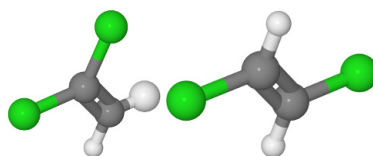
Figure 2.1: 1,1-dichloroethene and 1,2-dichloroethene.

(e) $CHCl_3$ chloroform is a dense sweet smelling liquid and is inactive, it boils at 61.15°C and the vapour is active, (f) H_2O vapour is active but not liquid water, (g) H_2O_2 when pure, is a viscous explosive liquid and cannot be vaporised without explosion and is normally used as a dilute solution in water and is inactive,
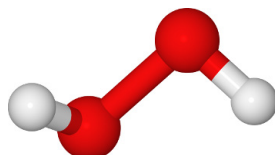
Figure 2.2: hydrogen peroxide.

(h) NH_3 ammonia vapour is active but ammonia liquid (boiling point -33.34°C) or as a solution in water is inactive.
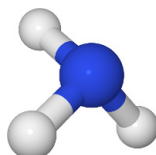
Figure 2.3: ammonia.

2.2   Solution

a) Assuming the rigid rotor approximation the gap between rotational levels is $2B$, and so the rotational constant is $B = 1.695$ cm^{-1}. (b) The rotational constant is $B = h/(8\pi^2 I c)$ cm^{-1} with c in cm s^{-1}.

$$I = \frac{h}{8\pi^2 c\, B} = \frac{6.6261\times 10^{-34}\,\text{J s}}{8\pi^2 \left(2.9979\times 10^{10}\,\text{cm s}^{-1}\right)\left(1.695\,\text{cm}^{-1}\right)} = 1.6515\times 10^{-46}\,\text{kg m}^2$$

b) The reduced mass μ is

$$\mu = \frac{m_N m_O}{m_N + m_O} = \frac{14.0031\times 15.9949}{14.0031 + 15.9949}\times 1.66054\times 10^{-27}\ \text{kg} = 1.2398\times 10^{-26}\ \text{kg}$$

c) The bond length r is related to the moment of inertia I via the reduced mass μ as below

$$I = \mu r_0^2 \qquad r_0 = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.6515\times 10^{-46}\,\text{kg m}^2}{1.2398\times 10^{-26}\,\text{kg}}} = 1.1542\times 10^{-10}\,\text{m} = 1.1542\,\text{Å}$$

Which to four significant figures, as in the original data, is $r_e = 1.154$ Å assuming it is the rigid-rotor. Note that for most non-organometallic molecules the values of moments of inertia are $I \approx 10^{-46}$ kg m^2, that reduced masses are $\mu \approx 10^{-26}$ kg and bond lengths are $r_0 \approx 1$–2 Å. If you get results much different from these values you should check carefully for a possible mistake.

2.3   Solution

The period of rotation of a molecule $\tau_{rot} \approx 10^{-11}$ s whereas the period of a bond vibration $\tau_{vib} \approx 10^{-13}$ s and during a typical rotation the molecule undergoes around 100 vibrations, so the bond length measured by MW spectroscopy is an average bond length averaged over many complete vibrations. As most molecules are in the ground vibrational level $v = 0$ the bond length is normally symbolised as r_0.

2.4   Solution

The ratio of the population is given by the Boltzmann distribution of energy levels.

$$\frac{P_{J=15}}{P_{J=7}} = \frac{g_{J=15}}{g_{J=7}}\exp\left(-\frac{E_{J=15} - E_{J=7}}{k_{\mathrm{B}}T}\right)$$

We can assume that NO is a rigid rotor then we can calculate the rotational energies using the rotational constant calculated in the question 2.1(a) $B = 1.695$ cm^{-1}. The degeneracy of a rotational level is $g_J = (2J+1)$ and the energy of a rotational level is $E_J = hcBJ(J+1)$ joules with c in cm s^{-1}.

$$\frac{P_{J=15}}{P_{J=7}} = \frac{2\times15+1}{2\times7+1}\exp\left(-\frac{hcB(15\times16) - hcB(7\times8)}{k_{\mathrm{B}}T}\right)$$

$$\frac{P_{J=15}}{P_{J=7}} = \frac{31}{15}\exp\left(-\frac{(6.6261\times10^{-34}\,\mathrm{J\,s})(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})(1.695\,\mathrm{cm^{-1}})\,184}{1.3807\times10^{-23}\,\mathrm{J\,K^{-1}}\times298.15\,\mathrm{K}}\right) = 0.4588$$

Don't confuse J the rotational quantum number (italic variable) with the units symbol for joules J (roman symbol or label), see (Parker 2013b). The NO molecule is slightly more than twice as likely to be in the rotational state with $J = 7$ at room temperature than in that with $J = 15$.

2.5   Solution

$$F(J) = J(J+1)B$$
$$\Delta F(3 \leftarrow 2) = (3 \times 4)B - (2 \times 3)B = 6B = 2 \text{ cm}^{-1} \quad \text{thus} \quad B = 0.3333 \text{ cm}^{-1}$$
$$\Delta F(8 \leftarrow 7) = (8 \times 9)B - (7 \times 8)B = 16 \times 0.3333 \text{ cm}^{-1} = 5.3328 \text{ cm}^{-1}$$

2.6   Solution

Note that microwave spectroscopy can measure line frequencies to 9 or 10 significant figures. We will temporary keep an excess number of significant figures for the intermediate calculation to reduce rounding errors and then correct the final result. Normally we work in wavenumbers (cm^{-1}) so we firstly convert the rotational constants in megahertz to wavenumbers.

	$^1\text{H}^{79}\text{Br}$	$^1\text{H}^{81}\text{Br}$	$^2\text{H}^{79}\text{Br}$	$^2\text{H}^{81}\text{Br}$
B_0/MHz	250357.599	250250.202	127357.6343	127279.7614

$$c = \lambda \nu \qquad \frac{1}{\lambda} = \frac{\nu}{c}$$

$$B(^1\text{H}^{79}\text{Br}) = \frac{250357.599 \times 10^6 \text{ s}^{-1}}{2.99792458 \times 10^{10} \text{ cm s}^{-1}} = 8.35103060 \text{ cm}^{-1}$$

$$B(^1\text{H}^{81}\text{Br}) = \frac{250250.202 \times 10^6 \text{ s}^{-1}}{2.99792458 \times 10^{10} \text{ cm s}^{-1}} = 8.34744822 \text{ cm}^{-1}$$

$$B(^2\text{H}^{79}\text{Br}) = \frac{127357.6343 \times 10^6 \text{ s}^{-1}}{2.99792458 \times 10^{10} \text{ cm s}^{-1}} = 4.24819341 \text{ cm}^{-1}$$

$$B(^2\text{H}^{81}\text{Br}) = \frac{127279.7614 \times 10^6 \text{ s}^{-1}}{2.99792458 \times 10^{10} \text{ cm s}^{-1}} = 4.24559584 \text{ cm}^{-1}$$

$$B = \frac{h}{8\pi^2 I c} \qquad I = \frac{h}{8\pi^2 B c}$$

$$I(^1\text{H}^{79}\text{Br}) = \frac{6.626068 \times 10^{-34} \text{J s}}{8\pi^2 (8.35103060 \text{ cm}^{-1})(2.99792458 \times 10^{10} \text{ cm s}^{-1})} = 3.35201056 \times 10^{-47} \text{ kg m}^2$$

$$I(^1\text{H}^{81}\text{Br}) = \frac{6.626068 \times 10^{-34} \text{ J s}}{8\pi^2 (8.34744822 \text{ cm}^{-1})(2.99792458 \times 10^{10} \text{ cm s}^{-1})} = 3.35344910 \times 10^{-47} \text{ kg m}^2$$

$$I(^2\text{H}^{79}\text{Br}) = \frac{6.626068 \times 10^{-34} \text{J s}}{8\pi^2 (4.24819341 \text{ cm}^{-1})(2.99792458 \times 10^{10} \text{ cm s}^{-1})} = 6.58932870 \times 10^{-47} \text{ kg m}^2$$

$$I(^2\text{H}^{81}\text{Br}) = \frac{6.626068 \times 10^{-34} \text{ J s}}{8\pi^2 (4.24559584 \text{ cm}^{-1})(2.99792458 \times 10^{10} \text{ cm s}^{-1})} = 6.59336023 \times 10^{-47} \text{ kg m}^2$$

Remember that an atom's mass is in kilograms not grams. To convert from atomic mass in g mol^{-1} or "u" to kilograms we multiply by the atomic mass constant (u). The quoted masses are to the appropriate number of places of experimental certainty, as Br is only known to 7 figures so the reduced mass will also be to 7 figures.

$$1\,\mathrm{u} = 1.6605387 \times 10^{-27}\,\mathrm{kg}$$

$$I = \frac{m_1 \times m_2}{m_1 + m_2}$$

$$\mu\left({}^{1}\mathrm{H}\,{}^{79}\mathrm{Br}\right) = \frac{1.007825032 \times 78.91833}{1.007825032 + 78.91833} \times 1.6605387 \times 10^{-27}\,\mathrm{kg} = 1.652430 \times 10^{-27}\,\mathrm{kg}$$

$$\mu\left({}^{1}\mathrm{H}\,{}^{81}\mathrm{Br}\right) = \frac{1.007825032 \times 80.91629}{1.007825032 + 80.916296} \times 1.6605387 \times 10^{-27}\,\mathrm{kg} = 1.652945 \times 10^{-27}\,\mathrm{kg}$$

$$\mu\left({}^{2}\mathrm{H}\,{}^{79}\mathrm{Br}\right) = \frac{2.014101777 \times 78.91833}{2.014101777 + 78.91833} \times 1.6605387 \times 10^{-27}\,\mathrm{kg} = 3.261262 \times 10^{-27}\,\mathrm{kg}$$

$$\mu\left({}^{2}\mathrm{H}\,{}^{81}\mathrm{Br}\right) = \frac{2.014101777 \times 80.91629}{2.014101777 + 80.916296} \times 1.6605387 \times 10^{-27}\,\mathrm{kg} = 3.263267 \times 10^{-27}\,\mathrm{kg}$$

$$I = \mu\,r^2 \qquad r = \sqrt{\frac{I}{\mu}}$$

$$r\left({}^{1}\mathrm{H}\,{}^{79}\mathrm{Br}\right) = \sqrt{\frac{3.35201056 \times 10^{-47}\,\mathrm{kg\,m}^2}{1.652430 \times 10^{-27}\,\mathrm{kg}}} = 1.424266 \times 10^{-10}\,\mathrm{m} = 1.424266\,\text{Å}$$

$$r\left({}^{1}\mathrm{H}\,{}^{81}\mathrm{Br}\right) = \sqrt{\frac{3.353449910 \times 10^{-47}\,\mathrm{kg\,m}^2}{1.652945 \times 10^{-27}\,\mathrm{kg}}} = 1.424350 \times 10^{-10}\,\mathrm{m} = 1.424350\,\text{Å}$$

$$r\left({}^{2}\mathrm{H}\,{}^{79}\mathrm{Br}\right) = \sqrt{\frac{6.58932870 \times 10^{-47}\,\mathrm{kg\,m}^2}{3.261262 \times 10^{-27}\,\mathrm{kg}}} = 1.421437 \times 10^{-10}\,\mathrm{m} = 1.421437\,\text{Å}$$

$$r\left({}^{2}\mathrm{H}\,{}^{81}\mathrm{Br}\right) = \sqrt{\frac{6.59336023 \times 10^{-47}\,\mathrm{kg\,m}^2}{3.263267 \times 10^{-27}\,\mathrm{kg}}} = 1.421435 \times 10^{-10}\,\mathrm{m} = 1.421435\,\text{Å}$$

The different isotopomers' bond lengths do not vary very much, only in the fourth decimal place for ${}^{1}\mathrm{H}{}^{79}\mathrm{Br}$ compared with ${}^{1}\mathrm{H}{}^{81}\mathrm{Br}$ and in the sixth decimal place for ${}^{2}\mathrm{H}{}^{79}\mathrm{Br}$ compared with ${}^{2}\mathrm{H}{}^{81}\mathrm{Br}$. Even though microwave spectroscopy can measure rotational constants to 9 or 10 significant figures remember the above calculation assumes the rigid rotor model and ignores the centrifugal distortion terms. The experimental values (Huber and Herzberg 1979 p. 276) are $r({}^{1}\mathrm{H}{}^{81}\mathrm{Br}) = 1.4144$, $r({}^{2}\mathrm{H}{}^{81}\mathrm{Br}) = 1.4145$ and $r({}^{3}\mathrm{H}{}^{81}\mathrm{Br}) = 1.4146$ Å so a high resolution absorption spectrum needs to take into account centrifugal distortion. Also the bond lengths calculated by the rigid rotor model as well as the experimental values are accurate values of an *average* bond length due to the vibrational motion of the bond.

2.7   Solution

The rotational constant is only quoted to 3 significant figures in the question which limits the precision of the moment of inertia and also the bond distance. First, the rigid rotor model has a constant spacing between neighbouring spectral lines.

$$
\begin{aligned}
&F(J) = BJ(J+1) \qquad F(J+1) = B(J+1)(J+2) \qquad F(J+2) = B(J+2)(J+3) \\
&\Delta F(J+1, J) = B(J+1)(J+2-J) = 2B(J+1) \\
&\Delta F(J+2, J+1) = B(J+2)(J+3-J-1) = 2B(J+2) \\
&\Delta F(J+2, J+1) - \Delta F(J+1, J) = 2B = 13.10\,\text{cm}^{-1} \quad \text{thus} \quad B = 6.55\,\text{cm}^{-1}
\end{aligned}
$$

This value for the rotational constant allows to find the average bond length r_0.

$$
\begin{aligned}
&B = \frac{h}{8\pi^2 I c} \qquad I = \frac{h}{8\pi^2 B c} \\
&I = \frac{6.6261 \times 10^{-34}\,\text{J s}}{8\pi^2 (6.55\,\text{cm}^{-1})(2.9979 \times 10^{10}\,\text{cm s}^{-1})} = 4.27 \times 10^{-47}\,\text{kg m}^2 \\
&\mu = \frac{1.007825 \times 126.9045}{1.007825 + 126.9045} \times 1.660539 \times 10^{-27}\,\text{kg} = 1.660347 \times 10^{-27}\,\text{kg} \\
&r = \sqrt{\frac{4.27 \times 10^{-47}\,\text{kg m}^2}{1.660347 \times 10^{-27}\,\text{kg}}} = 1.60 \times 10^{-10}\,\text{m} = 1.60\,\text{Å}
\end{aligned}
$$

2.8   Solution

As the bond length is given to 3 significant figures in the question so the moment of inertia, the rotational constant and the $\Delta F(5,4)$ are only given to 3 figures.

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2} = \frac{14.0031 \times 15.9949}{14.0031 + 15.9949} \times 1.6605 \times 10^{-27} \text{ kg} = 1.2398 \times 10^{-26} \text{ kg}$$

$$I = \mu\, r_0^2 = \left(1.2398 \times 10^{-26} \text{ kg}\right)\left(1.15 \times 10^{-10} \text{ m}\right)^2 = 1.64 \times 10^{-46} \text{ kg m}^2$$

$$B = \frac{h}{8\pi^2 I c} = \frac{6.6261 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{8\pi^2 \left(1.64 \times 10^{-46} \text{ kg m}^2\right)\left(2.9979 \times 10^{10} \text{ cm s}^{-1}\right)} = 1.71 \text{ cm}^{-1}$$

$$F(J) = B\, J\,(J+1)$$

$$\Delta F(5,4) = (B \times 5 \times 6) - (B \times 4 \times 5) = 10\,B = 17.1 \text{ cm}^{-1}$$

3 Vibrational Spectroscopy Tutorial

3.1 Question

Draw a typical potential energy curve as a function of internuclear distance for a diatomic molecule. Include on the drawing the allowed vibrational and rotational states. Describe how the potential and kinetic energies vary during the period of a complete vibration. On the sketch, show and differentiate between the bond dissociation energies D_e and D_0.

3.2 Question

State the specific selection rules for the gas-phase infrared vibration-rotation spectrum of HCl. Sketch and explain: (a) the energy level diagram and (b) the expected vibration-rotation spectrum for HCl.

3.3 Question

Which of the following molecules have a vibrational spectrum: (a) H_2, (b) HCl, (c) CO_2, (d) H_2O and (e) CH_4. How many fundamental modes of do each of the molecules have?

3.4 Question

A steel spring is fixed at one end to the ceiling of your lecture theatre and the other end has a 4 kg mass attached to it. If the spring is stretched and set into oscillation it has a frequency of 1.6 Hz, calculate the force constant of the spring.

3.5 Question

The fundamental vibration wavenumber of $^{35}Cl_2$ is $\bar{v}_e = 559.7$ cm^{-1}, as the molecule is a homonuclear diatomic this wavenumber was obtained from its Raman spectrum. Calculate the force constant of $^{35}Cl_2$.

3.6   Question

Explain the difference between overtone bands and hot bands in infrared spectroscopy. The fundamental and first overtone transitions of $^{12}C^{16}O$ are at 2143.2 cm^{-1} and 4259.9 cm^{-1}, respectively. Evaluate: (a) the equilibrium vibration wavenumber, $\bar{v}_e$ (b) the anharmonicity constant, x_e, (c) the anharmonic zero point energy and (d) the force constant of the molecule.

3.7   Question

CO_2 has a molar absorption coefficient of 2408 L mol^{-1} cm^{-1} at 2349 cm^{-1} due to the antisymmetric stretching mode. Although the CO_2 is in the gas phase and has a vibration-rotation spectrum we are not considering the rotational structure explicitly. Assuming an atmospheric CO_2 concentration of 397 parts per million (ppm) and an average troposphere air density of 1.204 g L^{-1} (20°C average temperature) calculate the concentration of CO_2 in mol L^{-1} and then the percentage of light absorbed for the antisymmetric stretching mode through atmospheric path lengths of (a) 1 cm, (b) 1 m and (c) 1 km. What conclusions do you draw from your calculations?

3.8   Question

The interhalogen molecule $^{127}I^{35}Cl$ boils at 96.98°C to forms a corrosive vapour which burns the skin and eyes. Its infrared spectrum gives $\bar{v}_e = 384.3$ cm^{-1} and $x_e\bar{v}_e = 1.501$ cm^{-1}. Calculate: (a) the force constant, (b) the wavenumber of the fundamental, (c) the wavenumber of the first overtone band and (d) the wavenumbers of the first hot band.

3.9   Question

How many fundamental vibrational modes do the following have: (a) H_2O_2, (b) C_6H_6, (c) HCN and (d) C_2H_2?

3.10   Question

Calculate the ratio of the populations of $v = 1$ to $v = 0$ at 298.15 K and 400 K for (a) Br_2 and (b) H_2 molecules assuming they are simple harmonic oscillators, Br_2 $\bar{v}_0 = 323.2$ cm^{-1} and H_2 $\bar{v}_0 = 4400.39$ cm^{-1}.

3.11   Question

The molecule $^{14}N^{16}O$ has an equilibrium vibration wavenumber $\bar{v}_e = 1904.2$ cm^{-1} and an anharmonicity term $x_e\bar{v}_e = 14.08$ cm^{-1}. Calculate the dissociation energy D_e assuming that the vibrational energy $G(v)$ is given by the Morse potential and then calculate D_0 giving any criticisms your method. Use 1 cm^{-1} = 11.958 kJ mol^{-1}.

3.1   Solution
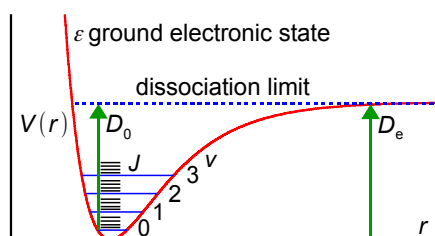
Figure 3.1: diatomic molecule PE curve, not to scale.

Fig. 3.1 is a potential energy curve, note the bond is harder to compress than to stretch, as shown by the steeper curve on the left hand side towards smaller internuclear separations. The bottom of the PE well has an energy $T_e = 0$ for the ground electronic state. The allowed vibrational states are shown by the blue horizontal lines, starting with $v = 0$ which is the zero point energy (ZPE) and increasing in steps ($v = 1, 2, 3, \ldots$) determined by the vibrational constant $\bar{v}_e$ and the anharmonicity constants $x_e\, y_e\, z_e$.

$$G(v) = \left(v + \tfrac{1}{2}\right)\bar{v}_e - \left(v + \tfrac{1}{2}\right)^2 \bar{v}_e\, x_e + \left(v + \tfrac{1}{2}\right)^3 \bar{v}_e\, y_e - \left(v + \tfrac{1}{2}\right)^4 \bar{v}_e\, z_e$$

Quite often we approximate this polynomial by using the quadratic two-term equation rather than the cubic or quartic versions. Each of the vibrational levels has a series of black rotational levels J so that in the gas phase a diatomic molecule can simultaneously change both v and J giving a vibration-rotation spectrum. The potential energy plateaus off at large internuclear separation as the potential energy becomes constant for the two non-interacting atoms. The dissociation energy D_0 measures the energy needed to take the molecule from the lowest energy level ($v = 0$) to infinite separation. The well depth D_e represents the energy from the bottom of the potential well ($T_e = 0$ for the ground electronic state) to infinite separation and is D_0 + ZPE.

In the course of a single vibration the potential and kinetic energies change as follows. Starting with $v = 0$ and the bond at maximum compression with minimum internuclear separation and the nuclei essentially stationary. This is to the left of the potential curve and all the vibrational energy is stored in the compressed bond as potential energy. The bond then lengthens, with potential energy being transformed into kinetic energy and the atoms moving faster and faster away from one another. At the equilibrium bond length r_e we reach the minimum potential energy where all of the vibrational energy has been converted to kinetic energy and the atoms are moving at their maximum velocity. The potential energy then starts increasing again as kinetic energy is converted into the stretching of the bond beyond the equilibrium length. We reach the maximum bond length when all of the kinetic energy has again been turned into potential energy this is exactly the same height up the curve as our starting point as total energy (kinetic plus potential) must be conserved at all times. The atoms then turn around and begin to accelerate together again. They once again pass through the equilibrium bond length at maximum velocity and climb the inner wall of the potential curve to return to the starting point of maximum potential energy. This completes one vibration. Because the vibrational potential plus vibrational kinetic energy is constant the total vibrational energy is a horizontal line. The symbols for vibrational energy are shown below.

$$E(v)\ \text{J} \quad \text{or} \quad G(v)\ \text{cm}^{-1}$$

3.2   Solution

HCl has only one vibrational mode which is parallel (symbol ∥) to the molecular axis. A parallel vibrational mode in the gas phase has the following specific selection rule.

$$\Delta v = \pm 1, \pm 2, \pm 3, \cdots \text{and} \, \Delta J = \pm 1$$

The rotational selection rule obeys the conservation of angular momentum. A photon has one unit of angular momentum ($1 \times h/2\pi$). HCl has a closed shell of electrons and zero electronic angular momentum. The only place that the absorbed photon's angular momentum can go is into the rotation of the molecule. It can either slow the rotation down or speed it up by one unit ($1 \times h/2\pi$) and in order to conserve angular momentum $\Delta J = \pm 1$. The existence of overtone transitions with $\Delta v > 1$ is the result of the anharmonicity of the vibration. Most molecules occupy $v = 0$ but a wide range of J levels and the selection rule simplifies.

$$\Delta v = +1 \, \text{and} \, \Delta J = \pm 1$$

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(a) The energy level diagram should look similar to Fig. 3.2. The rotational constants will be different in the upper and lower states, typically $B_0 > B_1$ as $r_0 < r_1$ due to the vibrational anharmonicity. (This is ignoring any breakdown of the Born-Oppenheimer approximation due to vibration-rotation coupling which gives an extra energy term $-h\alpha_e(v + \frac{1}{2})J(J + 1)$ where α_e is the vibration-rotation coupling constant which is much smaller than the rotational constant B_0.) In Fig. 3.2 the arrows drawn show the transitions allowed by the selection rules. They are labelled as P branch for $\Delta J = -1$ or R branch for $\Delta J = +1$. The subscript is J'' the lower rotational level quantum number.
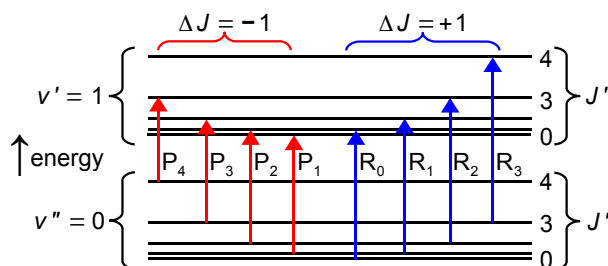

Figure 3.2: vibration-rotation energy levels, not to scale.

Vibration-rotation energy levels have the symbol $S(v, J)$ and ignoring centrifugal distortion we have.

$$S(v, J) = \left(v + \tfrac{1}{2}\right)\bar{v}_e - \left(v + \tfrac{1}{2}\right)^2 \bar{v}_e x_e + B_v J (J+1)$$
$$S(0, J'') = \tfrac{1}{2}\bar{v}_e - \tfrac{1}{4}\bar{v}_e x_e + B_0 J''(J''+1)$$
$$S(1, J') = \tfrac{3}{2}\bar{v}_e - \tfrac{9}{4}\bar{v}_e x_e + B_1 J'(J'+1)$$

(b) The IR vibration-rotation spectrum of HCl should look like Fig. 3.3. The R and P branches are spread out on either side of the band origin with the P branch on the low wavenumber side and the R branch on the high wavenumber side. The peaks are split as a result of the two ^{35}Cl and ^{37}Cl isotopes. The heavy mass of the Cl compared to the H atom means that the isotope shift is small, and in the real spectrum they are only just resolved. As J increases the R branch lines converge, whilst the P branch lines diverge. This is the result of the difference in B values for the upper and lower vibrational levels, $B_0 > B_1$. At high enough J values the R branch will display a band head.
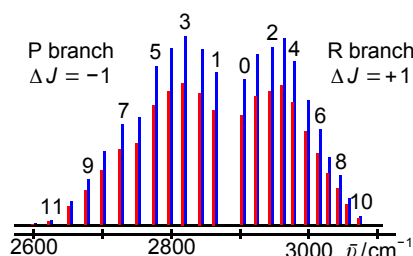

Figure 3.3: simulated HCl vibration-rotation spectrum.

33

The two isotopomer molecules have the same bond length and force constant but different reduced masses and hence different equilibrium vibration wavenumbers $\bar{v}_e$ which differ by about 2.2 cm^{-1} with the heavier molecule $^1H^{37}Cl$ (red) to lower wavenumber.

3.3   Solution

A molecule will have a vibrational spectrum where at least one of its vibrational modes has a change in dipole moment. The spectrum is "pure" if the molecule is in a condensed phase whereas in the gas phase it will be a vibration-rotation spectrum.

a) H_2 has one vibrational mode which does not change the dipole moment, IR inactive.

b) HCl is IR active, it is gaseous and has a PR parallel vibration-rotation spectrum, aqueous hydrochloric acid does has a pure vibrational stretching mode of its bond at 2990.95 cm^{-1}.

c) CO_2 has four vibrational modes and in the gas phase has a vibration-rotation spectrum. The symmetric stretching mode is IR inactive but from Raman spectroscopy is at 1340 cm^{-1}. The antisymmetric stretching mode is at 2349 cm^{-1} and the degenerate pair of bending modes are at 667 cm^{-1} and the latter three modes are IR active, but due to the degeneracy of the two bending modes there are two peaks in the spectrum.

d) H_2O liquid has a pure vibrational spectrum with the symmetric stretching mode at 3657 cm^{-1}. The antisymmetric stretching mode is at 3756 cm^{-1}. The bending mode at 1595 cm^{-1}.

e) CH_4 has 9 vibrational modes. The symmetric C-H stretching mode (at 2916 cm^{-1} from Raman spectroscopy) is IR inactive. Intense triply degenerate C-H stretching modes at 3019 cm^{-1}. An IR inactive C-H bending mode (at 1533 cm^{-1} from Raman). Finally there are intense triply degenerate C-H bending modes at 1311 cm^{-1}.

3.4   Solution

The mass of the lecture theatre (m_1) is much greater than 4 kg (m_2) so we have.

$$m_1 \gg m_2 \text{ and so } \mu = \frac{m_1 \times m_2}{m_1 + m_2} \approx \frac{m_1 \times m_2}{m_1} \approx m_2 \approx 4\,\text{kg}$$

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad k = 4\pi^2 v^2 \mu = 4\pi^2 (1.6\,\text{s}^{-1})^2 (4\,\text{kg}) = 404.3\,\text{kg s}^{-2} = 404.3\,\text{N m}^{-1}$$

3.5   Solution

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2} = \frac{34.9689 \times 34.9689}{34.9689 + 34.9689} \times 1.6605 \times 10^{-27}\,\text{kg} = 2.9033 \times 10^{-26}\,\text{kg}$$

$$\bar{v}_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad k = 4\pi^2 \bar{v}_e^{\,2} c^2 \mu$$

$$k = 4\pi^2 \left(559.7\,\text{cm}^{-1}\right)^2 \left(2.9979 \times 10^{10}\,\text{cm s}^{-1}\right)^2 \left(2.9033 \times 10^{-26}\,\text{kg}\right) = 322.7\,\text{N m}^{-1}$$

3.6   Solution

Overtone bands arise from transitions with $\Delta v = \pm 2, \pm 3, \ldots$ and they are forbidden for a simple harmonic oscillator, but are allowed as a result of the anharmonicity of real potential energy curves. Overtone bands are significantly weaker than the fundamental $\Delta v = \pm 1$ transition and occur at approximate multiples of the fundamental wavenumber $\bar{v}$.

Hot band absorptions are all $\Delta v = +1$ arising from vibrational levels other than the ground vibrational level, *e.g.* the first hot band is $\Delta v_{2,1}$ and the second hot band is $\Delta v_{3,2}$. They are generally much weaker than the fundamental as the large vibrational energy spacing compared with thermal energies results in negligible population of excited vibrational levels at room temperature as given by the Boltzmann distribution. Hot bands will only be significant at elevated temperatures, or for molecules with very low vibrational wavenumbers such as I_2 with $\bar{v}_e = 214.5$ cm^{-1} where a significant excited state population exists even at 298 K. Hot bands are all close to, but less than, the fundamental transition $\Delta v_{1,0}$.

(a) and (b)

$$G_v = \left(v + \tfrac{1}{2}\right)\bar{v}_e - \left(v + \tfrac{1}{2}\right)^2 x_e \bar{v}_e$$

$$G_0 = \tfrac{1}{2}\bar{v}_e - \tfrac{1}{4}x_e\bar{v}_e \qquad G_1 = \tfrac{3}{2}\bar{v}_e - \tfrac{9}{4}x_e\bar{v}_e \qquad G_2 = \tfrac{5}{2}\bar{v}_e - \tfrac{25}{4}x_e\bar{v}_e$$

$$\Delta G_{1,0} = \bar{v}_e - 2x_e\bar{v}_e = 2143.2\,\text{cm}^{-1} \qquad \Delta G_{2,0} = 2\bar{v}_e - 6x_e\bar{v}_e = 4259.9\,\text{cm}^{-1}$$

$$3\Delta G_{1,0} - \Delta G_{2,0} \text{ gives } \bar{v}_e = 2169.7\,\text{cm}^{-1}$$

$$2\Delta G_{1,0} - \Delta G_{2,0} \text{ gives } 2x_e\bar{v}_e = 26.5\text{ cm}^{-1} \quad x_e = 6.1068\times10^{-3}$$

(c) The zero point energy is the energy of the lowest vibrational level, $v = 0$.

$$G_0 = \tfrac{1}{2}\bar{v}_e - \tfrac{1}{4}x_e\bar{v}_e = \tfrac{1}{2}\times2169.7\,\text{cm}^{-1} - \tfrac{1}{4}\times13.25\,\text{cm}^{-1} = 1081.5\,\text{cm}^{-1}$$

(d) The force constant of the molecule k is related to the vibrational wavenumber and reduced mass μ.

$$\mu = \frac{m_O \times m_C}{m_O + m_C} = \frac{15.9949\times12.0000}{15.9949 + 12.0000}\times1.6605\times10^{-27}\text{ kg} = 1.1385\times10^{-26}\text{ kg}$$

$$\bar{v}_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad k = 4\pi^2 c^2 \bar{v}_e^{\,2}\mu$$

$$k = 4\pi^2 (2.9979\times10^{10}\text{ cm s}^{-1})^2 (2169.7\text{ cm}^{-1})^2 (1.1385\times10^{-26}\text{ kg}) = 1901.6\text{ N m}^{-1}$$

3.7   Solution

$$[CO_2] = \frac{397\,\text{g CO}_2}{1\times10^6\,\text{g air}} = \frac{397\,\text{g CO}_2/44.01\,\text{g mol}^{-1}}{1\times10^6\,\text{g air}/1.204\,\text{g L}^{-1}} = \frac{9.0207\,\text{mol CO}_2}{8.3056\times10^5\,\text{L air}} = 1.0861\times10^{-5}\,\text{mol L}^{-1}$$

$$A = \varepsilon\,c\,l = (2408\,\text{L mol}^{-1}\text{cm}^{-1})(1.0861\times10^{-5}\,\text{mol L}^{-1})(1\,\text{cm}) = 0.02615$$

$$A = \log\frac{I_0}{I} = \log\frac{100}{I} = 0.02615 \qquad I = 94.16\,\% \qquad\qquad \text{absorbed in 1 cm} = 5.84\,\%$$

$$A = \varepsilon\,c\,l = (2408\,\text{L mol}^{-1}\text{cm}^{-1})(1.0861\times10^{-5}\,\text{mol L}^{-1})(100\,\text{cm}) = 2.6153$$

$$A = \log\frac{I_0}{I} = \log\frac{100}{I} = 2.6153 \qquad I = 0.2425\,\% \qquad\qquad \text{absorbed in 1 m} = 99.76\,\%$$

$$A = \varepsilon\,c\,l = (2408\,\text{L mol}^{-1}\text{cm}^{-1})(1.0861\times10^{-5}\,\text{mol L}^{-1})(10^5\,\text{cm}) = 2.6153\times10^3$$

$$A = \log\frac{I_0}{I} = \log\frac{100}{I} = 2.6153\times10^3 \qquad I = 0\,\% \qquad\qquad \text{absorbed in 1 km} = 100\,\%$$

Note that 1 km path length (to the precision of my calculator) is 100% absorbed. This is due to the logarithmic form of the Beer-Lambert law. So the take home message for global warming is that it is *not* the absorption at the peak of the IR absorption curve(s) that is the problem, as that is already fully saturated but it is the *edges* of the peaks and the weak overtone and weak combination bands which are the problem with the extra CO_2 we are pumping into the atmosphere. These "off-peak" absorptions are weak enough that more CO_2 concentration will result in more IR absorbed and therefore more heating. This is often a reason for the sceptics and deniers failure to realize what is going on in climate modelling.

3.8   Solution

$$\text{(a) } \mu = \frac{m_{127}\times m_{35}}{m_{127}+m_{35}} = \frac{126.904\times34.9689}{126.904+34.9689}\times1.6605\times10^{-27}\,\text{kg} = 4.55221\times10^{-26}\,\text{kg}$$

$$\bar{v}_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad k = 4\pi^2 c^2 \bar{v}_e^{\,2}\mu$$

$$k = 4\pi^2(2.998\times10^{10}\,\text{cm s}^{-1})^2(384.3\,\text{cm s}^{-1})^2(4.55221\times10^{-26}\,\text{kg}) = 238.55\,\text{N m}^{-1}$$

Note that the ^{127}I^{35}Cl has a very flexible "floppy" bond.
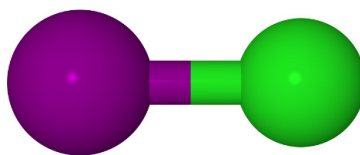
Figure 3.4: iodine chloride.

$$\text{(b) } G_v = \left(v+\tfrac{1}{2}\right)\bar{v}_e - \left(v+\tfrac{1}{2}\right)^2 x_e\,\bar{v}_e \qquad\qquad G_0 = \tfrac{1}{2}\times384.3\,\text{cm}^{-1} - \tfrac{1}{4}\times1.501\,\text{cm}^{-1}$$

$$G_1 = \tfrac{3}{2}\times384.3\,\text{cm}^{-1} - \tfrac{9}{4}\times1.501\,\text{cm}^{-1} \qquad G_2 = \tfrac{5}{2}\times384.3\,\text{cm}^{-1} - \tfrac{25}{4}\times1.501\,\text{cm}^{-1}$$

$$\Delta G_{1,0} = 384.3\,\text{cm}^{-1} - 2\times1.501\,\text{cm}^{-1} = 381.3\,\text{cm}^{-1}$$

The fundamental wavenumber is small due to the low value of the force constant and the vibrational levels are closely spaced.

$$\text{(c)} \; \Delta G_{2,0} = 2 \times 384.3 \, \text{cm}^{-1} - 6 \times 1.501 \, \text{cm}^{-1} = 759.6 \, \text{cm}^{-1}$$

The first overtone is slightly less than twice the fundamental wavenumber and its intensity relative to the fundamental is temperature independent.

$$\text{(d)} \; \Delta G_{2,1} = 384.3 \, \text{cm}^{-1} - 4 \times 1.501 \, \text{cm}^{-1} = 378.3 \, \text{cm}^{-1}$$

The first hot band is slightly below the wavenumber of the fundamental transition and its intensity relative to the fundamental is low but temperature dependent.

3.9   Solution

Non-linear molecules have $(3N - 6)$ modes and linear molecules have $(3N - 5)$ modes.

(a) H_2O_2	$N = 4$	$(3N-6) = 6$	(b) C_6H_6	$N = 12$	$(3N-6) = 30$
(c) HCN	$N = 3$	$(3N-5) = 4$	(d) C_2H_2	$N = 4$	$(3N-5) = 7$

3.10   Solution

At 298.15 K the conversion factor $k_B T/hc$ = 207.2 cm^{-1} and so we can find that at 400 K the conversion factor is $k_B T/hc$ = 207.2 cm^{-1}×(400 K/298.15 K) = 278.0 cm^{-1}.

Boltzmann distribution: $\dfrac{n_1}{n_0} = \exp\left(-\dfrac{\bar{v}_0 h c}{k_B T}\right)$

(a) Br_2 at 298.15 K: $\dfrac{n_1}{n_0} = \exp\left(-\dfrac{323.2\,\mathrm{cm}^{-1}}{207.2\,\mathrm{cm}^{-1}}\right) = 0.2102$ 21.02%

Br_2 at 400 K: $\dfrac{n_1}{n_0} = \exp\left(-\dfrac{323.2\,\mathrm{cm}^{-1}}{278.0\,\mathrm{cm}^{-1}}\right) = 0.3127$ 31.27%

(b) H_2 at 298.15 K: $\dfrac{n_1}{n_0} = \exp\left(-\dfrac{4400.39\,\mathrm{cm}^{-1}}{207.2\,\mathrm{cm}^{-1}}\right) = 5.980\times10^{-10} \approx 0\%$

H_2 at 400 K: $\dfrac{n_1}{n_0} = \exp\left(-\dfrac{4400.39\,\mathrm{cm}^{-1}}{278.0\,\mathrm{cm}^{-1}}\right) = 1.336\times10^{-7} \approx 0\%$

Note that molecules with low wavenumber vibrations less than about 700 cm^{-1} have appreciable populations in excited vibrational levels. Those molecules with high wavenumber vibrations more than around 700 cm^{-1} are essentially all in the ground vibrational level even at higher temperatures. Secondly $k_B T/hc$ can easily be calculated at any temperature by knowing its value at 298.15 K.

3.11 Solution

$$G_V = \left(v + \tfrac{1}{2}\right)\bar{v}_e - \left(v + \tfrac{1}{2}\right)^2 \bar{v}_e x_e = \left(v + \tfrac{1}{2}\right)\bar{v}_e - \left(v^2 + v + \tfrac{1}{4}\right)\bar{v}_e x_e$$

$$G_{V+1} = \left(v + \tfrac{3}{2}\right)\bar{v}_e - \left(v + \tfrac{3}{2}\right)^2 \bar{v}_e x_e = \left(v + \tfrac{3}{2}\right)\bar{v}_e - \left(v^2 + 3v + \tfrac{9}{4}\right)\bar{v}_e x_e$$

$$\Delta G_{V+1,V} = \bar{v}_e - \left(2v+2\right)\bar{v}_e x_e \qquad \left(2v_{max}+2\right)\bar{v}_e x_e = \bar{v}_e \qquad 2v_{max}\bar{v}_e x_e = \bar{v}_e - 2\bar{v}_e x_e$$

$$v_{max} = \frac{1}{2x_e} - 1 = \frac{1}{2\times(14.08\,\text{cm}^{-1}/1904.2\,\text{cm}^{-1})} - 1 = \frac{1}{2\times 7.3942\times 10^{-3}} - 1 = 66.6$$

The vibrational levels are quantized so $v_{max} = 66.6$ let us assume $v_{max} = 66$.

$$D_e = G_{V_{max}} = \left(66 + \tfrac{1}{2}\right)1904.2\ \text{cm}^{-1} - \left(66 + \tfrac{1}{2}\right)^2 14.08\ \text{cm}^{-1} = 64364\ \text{cm}^{-1}$$

$$G_0 = \tfrac{1}{2}\times 1904.2\,\text{cm}^{-1} - \tfrac{1}{4}\times 14.08\,\text{cm}^{-1} = 948.6\,\text{cm}^{-1}$$

$$D_0 = D_e - G_0 = 63415\ \text{cm}^{-1}$$

The Morse potential is only an approximation to the true PE curve of a diatomic molecule. Its advantage is that it is analytically simple and inserting it into the Schrödinger equation leads to the well known solutions for G_v shown on the first line of the solution and below. A better agreement with the experimental PE curve is found by fitting the empirical dimensionless parameters $x_e\,y_e\,z_e$ to the vibrational energy levels.

Morse vibrational levels: $\quad G_V = \left(v + \tfrac{1}{2}\right)\bar{v}_e - \left(v + \tfrac{1}{2}\right)^2 \bar{v}_e x_e$

Empirical vibrational levels: $\quad G_V = \left(v + \tfrac{1}{2}\right)\bar{v}_e - \left(v + \tfrac{1}{2}\right)^2 \bar{v}_e x_e + \left(v + \tfrac{1}{2}\right)^3 \bar{v}_e y_e - \left(v + \tfrac{1}{2}\right)^4 \bar{v}_e z_e$

The value obtained for the dissociation energy using the Morse potential will be an overestimate of the experimental value. If the dissociation limit of the upper state is not within the Franck-Condon region then a better treatment is the Birge-Sponer extrapolation, see Parker (Parker, 2013a, p. 19). If the dissociation limit is accessible within the Franck-Condon region then the purely experimental spectroscopic measurements gives the true dissociation limit.

4 Raman Spectroscopy Tutorial

4.1 Question

Which of the following molecules have a rotational spectrum in the microwave and which are rotationally Raman active: (a) H_2, (b) CH_4, (c) SF_6, (d) HCl, (e) O_2?

4.2 Question

Which of the three vibrational modes of H_2O and the four of CO_2 are IR active and Raman active?

4.3   Question

Using a nitrogen laser of 337.1 nm wavelength it is found that the $^1H^{35}Cl$ molecule has a rotational constant of $B = 10.593$ cm^{-1}. Predict the positions of the first four Stokes and first four ant-Stokes lines in the rotational Raman spectrum.

4.4   Question

Using a nitrogen laser of 337.1 nm wavelength it is found that the $^1H^{35}Cl$ molecule has a vibrational equilibrium wavenumber of $\bar{v}_e = 2990.95$ cm^{-1} and an anharmonicity term $\bar{v}_e x_e = 52.82$ cm^{-1}. Predict the positions of the Stokes and anti-Stokes fundamental and first overtone lines in the pure vibrational Raman spectrum.

4.5   Question

The homonuclear diatomic molecule $^{19}F_2$ does not have an IR absorption. If the rotational Raman spectrum has a series of Stokes and anti-Stokes lines separated by 3.5312 cm^{-1} calculate the bond length of $^{19}F_2$.

4.1   Solution

The Raman exclusion rule helps with this question.

> For a molecule with an inversion centre a mode cannot be both Raman and IR active, however, it may be inactive in both

a) H_2 has zero dipole moment, it is MW inactive, rotation gives a change in polarizability, Raman rotationally active.

b) CH_4 is a spherical rotor with zero dipole moment, it is MW inactive, there is no change in polarizability as it rotates and it is also Raman rotationally inactive.

c) SF_6 is a spherical rotor with zero dipole moment, it is MW inactive, there is no change in polarizability as it rotates and it is also Raman rotationally inactive.

d) HCl has a dipole moment and is MW active, rotation gives a change in polarizability, Raman rotationally active.

e) O_2 has zero dipole moment and is MW inactive, rotation gives a change in polarizability, Raman rotationally active.

4.2   Solution

H_2O does not have a centre of symmetry and the decision on Raman activity is whether the molecule changes its polarizability during a given vibrational mode. The symmetric stretching, antisymmetric stretching and bending mode of H_2O are all IR active as the dipole moment changes. The three modes also have a change in the polarizability and they are all vibrationally Raman active.

CO_2 has a centre of symmetry and the analysis is more involved and less obvious (Parker 2015, section 5.2). The symmetric stretching mode there is no change in dipole moment and it is IR inactive. For *small* extensions the molecule's polarizability α increases as the displacement ε (the total bond length) increases from the equilibrium position as the molecule stretches. The polarizability α decreases as the displacement ε contracts from the equilibrium position so the differential $d\alpha/d\varepsilon \neq 0$ at $\varepsilon = 0$ for the symmetric stretching mode of CO_2 is vibrationally Raman active.
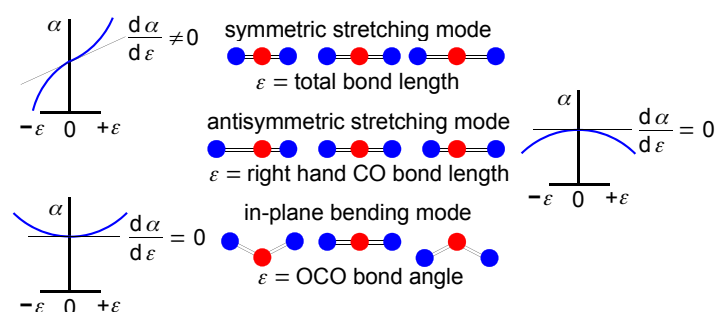
Figure 4.1: polarizability α versus displacement ε for CO_2 vibration modes.

In the antisymmetric stretching mode of CO_2 the molecule's polarizability α decreases as the displacement ε (the right hand CO bond length) increases from the equilibrium position. However, the polarizability α also decreases as the displacement ε decreases the right hand CO bond from the equilibrium position. So for *small* extensions $d\alpha/d\varepsilon = 0$ at $\varepsilon = 0$ and the antisymmetric stretching mode is vibrationally Raman inactive.

The degenerate bending modes of CO_2 the polarizability α increases as the displacement ε (the OCO bond angle) increases from the equilibrium position. However, the polarizability α also increases as the displacement ε decreases from the equilibrium position. For *small* extensions $d\alpha/d\varepsilon = 0$ at $\varepsilon = 0$ and the bending modes are vibrationally Raman inactive.

4.3   Solution

$\Delta J = 0, \pm 2$ for a linear rotor but $\Delta J = 0$ does not change the wavenumber
$\Delta J = 0$ is the Rayleigh scattering

Stokes lines are $\Delta J = +2$ that is $(J+2 \leftarrow J)$

$$\bar{v}_{\text{Stokes}} = \bar{v}_i - (F_{J+2} - F_J) = \bar{v}_i - \left[B(J+2)(J+3) - BJ(J+1) \right] = \bar{v}_i - B(4J+6)$$

J	0	1	2	3	…
$\bar{v}_{\text{Stokes}}$	$\bar{v}_i - 6B$	$\bar{v}_i - 10B$	$\bar{v}_i - 14B$	$\bar{v}_i - 18B$	…

The N_2 laser wavelength of 337.1 nm is 29665 cm^{-1}. The rotational Raman Stokes lines are 29601, 29559, 29517 and 29474 cm^{-1} with a gap of $4B$ between them and all of them in the UV.

anti-Stokes lines are $\Delta J = -2$ that is $(J-2 \leftarrow J)$

$$\bar{v}_{\text{anti-Stokes}} = \bar{v}_i + (F_J - F_{J-2}) = \bar{v}_i + BJ(J+1) - B(J-2)(J-1) = \bar{v}_i + B(4J-2)$$

J	2	3	4	5	…
$\bar{v}_{\text{anti-Stokes}}$	$\bar{v}_i + 6B$	$\bar{v}_i + 10B$	$\bar{v}_i + 14B$	$\bar{v}_i + 18B$	…

The anti-Stokes lowest transition starts from $J = 2$. The rotational Raman Stokes lines are 29729, 29771, 29813 and 29856 cm^{-1} with a gap of $4B$ between them and all of them in the UV.

Figure 4.2: linear molecule rotational Raman transitions.

4.4   Solution

$^1H^{35}Cl$ has only one mode with a large vibration wavenumber, so in the condensed phase we expect to see the fundamental and the first overtone but not the hot hands at ambient temperatures. The specific selection rule for vibrational Raman spectra is the same as the IR selection rule.

$\Delta v = 0, \pm 1, \pm 2, \pm 3, \cdots$ with the transition probability decreasing rapidly, but
$\Delta v = 0$ does not change the wavenumber, *Rayleigh scattering*
$\Delta v = \pm 1$ with plus sign the Stokes and minus sign the anti-Stokes *fundamentals*
$\Delta v = \pm 2$ with plus sign the Stokes and minus sign the anti-Stokes *overtones*

Fundamental: $v(1 \leftarrow 0)$
$\Delta \bar{v}_{\text{fundamental}} = \left(\frac{3}{2}\bar{v}_e - \frac{9}{4}\bar{v}_e x_e\right) - \left(\frac{1}{2}\bar{v}_e - \frac{1}{4}\bar{v}_e x_e\right) = \left(\bar{v}_e - 2\bar{v}_e x_e\right)$
$\Delta \bar{v}_{\text{fundamental}} = 2990.95 \text{ cm}^{-1} - 2\times 52.82 \text{ cm}^{-1} = 2885.31 \text{ cm}^{-1}$
Overtone: $v(2 \leftarrow 0)$
$\Delta \bar{v}_{\text{overtone}} = \left(\frac{5}{2}\bar{v}_e - \frac{25}{4}\bar{v}_e x_e\right) - \left(\frac{1}{2}\bar{v}_e - \frac{1}{4}\bar{v}_e x_e\right) = \left(2\bar{v}_e - 6\bar{v}_e x_e\right)$
$\Delta \bar{v}_{\text{overtone}} = 2\times 2990.95 \text{ cm}^{-1} - 6\times 52.82 \text{ cm}^{-1} = 5664.98 \text{ cm}^{-1}$

The N_2 laser line is at 337.1 nm which is 29665 cm^{-1}. The pure vibrational Raman fundamental Stokes line is at 26780 and the fundamental anti-Stokes is at 32550 cm^{-1}. The pure vibrational overtone Raman Stokes line is at 24000 and the anti-Stokes is at 35330 cm^{-1} all of them in the UV. In the gas phase each vibrational Raman line has rotational Raman fine structure.
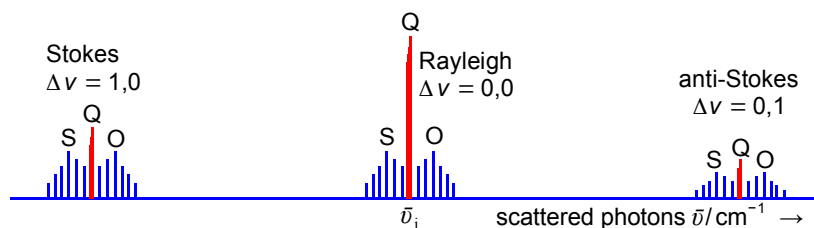
Figure 4.3: vibrational-rotational Raman transitions, energy not to scale for clarity.

4.5 Solution

The lines in the rotational Raman spectrum are separated by $4B$ and so $B = 0.8828$ cm^{-1} for the ^{19}F$_2$ molecule.

$$\mu = \frac{18.998 \times 18.998}{18.998 + 18.998} \times 1.6605 \times 10^{-27}\,\text{kg} = 1.5773 \times 10^{-26}\,\text{kg}$$

$$B = \frac{h}{8\pi^2 c \mu r^2} \qquad r = \sqrt{\frac{h}{8\pi^2 c \mu B}}$$

$$r = \sqrt{\frac{6.626 \times 10^{-34}\,\text{J s}}{8\pi^2 (2.998 \times 10^{10}\,\text{cm s}^{-1})(1.5773 \times 10^{-26}\,\text{kg})(0.8828\,\text{cm}^{-1})}} = 1.418 \times 10^{-10}\,\text{m}$$

The bond length in the ground vibrational state is $r_0 = 1.418$ Å.

5 Atomic Spectroscopy Tutorial

5.1 Question

The Paschen series of the H-atom involves transitions from $n = 3$ to higher levels.

a) What is the energy of this level according to the Bohr model of the H-atom?
b) What defines the zero of energy for this energy?
c) What is the lowest energy transition of the Paschen series?
d) What is the wavelength of the light for this transition?
e) What region of the electromagnetic spectrum does this wavelength lie?

5.2 Question

a) Write down the electron configurations of the ground states of Li and Na atoms.
b) State Pauli's exclusion principle for electrons in atomic orbitals. How many electrons can be accommodated in the 4d orbitals?

c) Arsenic has atomic number $Z = 33$, predict the ground state electron configuration for the As atom according to the aufbau principle.

d) State Hund's rule of maximum multiplicity and sketch the lowest energy orbital diagram for As indicating clearly the values of n, l and m_l for all orbitals in your diagram.

e) The standard enthalpy of ionization (also called the ionization energy) of As is $\Delta H^o_{ion} = 947$ kJ mol^{-1}. From which orbital is the electron ejected in this ionization? If the ionization is caused by UV photons with a wavelength 58.4 nm, what is the maximum kinetic energy of the electrons that are ejected?

f) Predict a valid orbital diagram for the ground states of both N and Si atoms. Label all the occupied orbitals clearly.

g) How many orbital diagrams of equal energy are there for the ground states of C and O atoms?

h) How do the energies of atomic orbitals depend on n and l? Distinguish carefully between the H and He atoms, including sketches of the relative energies of all the orbitals up to $n = 3$ for H and He.

5.3 Question

Which of the following sets of quantum numbers are valid? For invalid sets explain why they are invalid. Point out also those sets that actually exist in nature. (a) $n = 3$, $l = 3$, $m_l = 0$; (b) $n = 2$, $l = 1$, $m_l = 0$; (c) $n = 6$, $l = 5$, $m_l = \pm 1$ and (d) $n = 4$, $l = 3$, $m_l = \pm 4$.

5.4 Question

Sodium street lights have a doublet of lines at 588.9950 nm and 589.5924 nm. What is the energy difference between these lines in J mol^{-1}.

5.5 Question

a) For the Russell-Saunders term symbol $^4D_{5/2}$ determine the values of the quantum numbers S, L and J.

b) Determine the minimum number of electrons that could form this $^4D_{5/2}$ state.

c) With this minimum number of non-equivalent electrons, find possible electron configurations for this $^4D_{5/2}$ state.

5.6 Question

a) Find the term symbol of the ground electron configuration of the sodium atom Na $1s^2 2s^2 2p^6 3s^1$.
b) Find the term symbol of the excited electron configuration of the sodium atom Na $1s^2 2s^2 2p^6 3s^0 3p^1$.
c) Which of the three possible transitions involving the excited states and ground state is forbidden by the Russell-Saunders selection rules and for what reason?

5.7 Question

a) What is the term symbol for the ground electron configuration of the C-atom $1s^2 2s^2 2p^2$?
b) In flames and electric discharges carbon give excited C-atom with an electron configuration of $1s^2 2s^2 2p^1 3p^1$. What are the term symbols for this electron configuration.

5.1 Solution

$$(a)\ E(n) = -\frac{R_\mathrm{H}}{n^2} \quad R_\mathrm{H} \text{ is the Rydberg constant for the H-atom}$$

$$E(3) = -\frac{1.0974 \times 10^5\,\mathrm{cm}^{-1}}{3^2} = -1.219 \times 10^4\,\mathrm{cm}^{-1}$$

The energy of the electron is negative as it is measured relative to zero which is defined as an isolated electron not bound in the atom, which is now a cation. So the atomic electron has a lower energy than the free electron, it is negative. (b) The lowest energy transition is from $n = 3$ to the next level $n = 4$ and the energy of this transition is the energy difference between the two levels.

$$(c)\ \Delta E(4 \leftarrow 3) = \left(-\frac{R_\mathrm{H}}{4^2}\right) - \left(-\frac{R_\mathrm{H}}{3^2}\right) = -R_\mathrm{H}\left(\frac{1}{16} - \frac{1}{9}\right) = -R_\mathrm{H}\left(-4.8611 \times 10^{-2}\right)$$

$$\Delta E(4 \leftarrow 3) = 109737\ \mathrm{cm}^{-1} \times 4.8611 \times 10^{-2} = 5334.4\ \mathrm{cm}^{-1}$$

$$(d)\ \lambda = \frac{1}{5334.4\,\mathrm{cm}^{-1} \times 100\,\mathrm{cm\ m}^{-1}} = 1.8746\ \mu\mathrm{m}$$

An IR photon is absorbed by the H-atom which jumps from $n = 3$ to $n = 4$.

5.2   Solution

a) Li ($Z = 3$) ground electron configuration $1s^2 2s^1$ and Na ($Z = 11$) has a ground electron configuration $1s^2 2s^2 2p^6 3s^1$.

b) Pauli's exclusion principle states that no two electrons in an atom can have the same set of four quantum numbers n, l, m_l and m_s. An orbital is defined by a unique combination of n, l and m_l, this means that the two electrons in an orbital must have different values of m_s. There are only two possible values of $m_s = \pm\frac{1}{2}$, so at most two electrons can be accommodated in an orbital and they must have opposite spins. The 4d subshell has $l = 2$ so there are $(2l+1) = 5$ values of m_l and these five orbitals which can hold up to 10 electrons.

c) Following the normal sequence for filling the orbitals according to the aufbau principle, in English "building-up", (also called the Madelung rule, the diagonal rule or the $n+l$ rule) where electrons fill up the subshells in the order of the arrows (order of $n+l$) in Fig. 5.1.
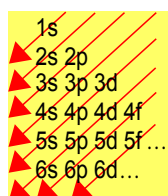

Figure 5.1: Madelung, diagonal or ($n+l$) rule for energy ordering.

Arsenic (Z = 33) fills the subshells in the order $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$ (note the order of 4s, 3d and 4p). Conventionally these are then quoted in the order of the shells (by the principal quantum number) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$ for the ground configuration of As.

d) Hund's rule of maximum multiplicity states that in the ground state of an atom the electrons in the outer partially filled subshell are organised to maximize the overall spin. This corresponds to the maximum number of different orbitals of the same n and l and different m_l being filled with single electrons with parallel spins before any orbitals are doubly occupied with paired spins. Hence for As the ground state orbital diagram is shown below with three parallel unpaired 4p electrons.
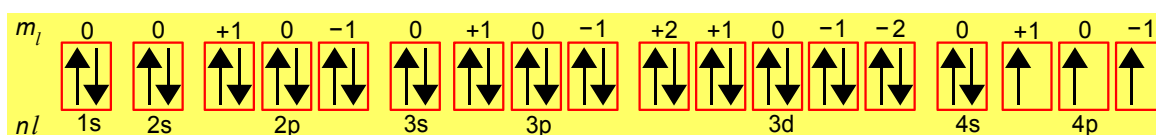
Figure 5.2: arsenic atom orbital diagram.

e) The electron is ejected from the highest energy occupied atomic orbital, therefore from any one of the 4p orbitals (all three m_l have the same energy). The maximum kinetic energy of the electron is the difference between the photon energy and the first ionization energy. The ionization energy per atom is calculated first.

$$\Delta H^{\circ}_{\text{ion atom}} = \frac{\Delta H^{\circ}_{\text{ion mol}}}{N_A} = \frac{947 \times 10^3 \, \text{J mol}^{-1}}{6.022 \times 10^{23} \, \text{mol}^{-1}} = 1.573 \times 10^{-18} \, \text{J}$$

We then convert the photon wavelength to a photon energy.

$$c = \lambda \nu \qquad E_{\text{photon}} = h \nu$$
$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \, \text{J s})(2.998 \times 10^8 \, \text{m s}^{-1})}{58.4 \times 10^{-9} \, \text{m}} = 3.401 \times 10^{-18} \, \text{J}$$

Subtracting the ionization energy from the photon energy gives the kinetic energy of the ejected electron.

$$E_{\text{electron}} = (3.401 \times 10^{-18} \, \text{J}) - (1.573 \times 10^{-18} \, \text{J}) = 1.828 \times 10^{-18} \, \text{J}$$
$$E_{\text{electron}} = (1.828 \times 10^{-18} \, \text{J})(6.022 \times 10^{23} \, \text{mol}^{-1}) = 1101 \, \text{kJ mol}^{-1}$$
$$E_{\text{electron}} = \frac{1.828 \times 10^{-18} \, \text{J}}{1.60219 \times 10^{-19} \, \text{J/eV}} = 11.41 \, \text{eV}$$

f) The N-atom ($Z = 7$) has an electron configuration of $1s^2 2s^2 2p^3$. According to Hund's rule of maximum multiplicity, the three electrons in the 2p shell will occupy three separate p orbitals *i.e.* have different values of m_l with parallel spins. The orbital diagram is below.
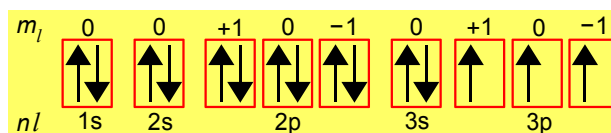
Figure 5.3: nitrogen atom orbital diagram.

There is nothing special about spin up versus spin down, so an equally valid diagram would have 3 parallel spin down electrons in the 2p orbitals. The Si-atom ($Z = 14$) has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^2$. A valid orbital diagram for the ground state is one in which the two 3p electrons occupy different orbitals with the same spin or any other combination of two different m_l values with parallel up or down spins, so there a total of six valid orbital diagrams.
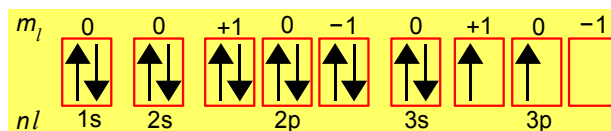
Figure 5.3: silicon atom orbital diagram.

g) The C-atom ($Z = 6$) has an electron configuration of $1s^2 2s^2 2p^2$. The outer p^2 configuration (which is the same as Si because they are in the same group) will have 2 parallel spins in different orbitals, which can be achieved by leaving any one p orbital empty. This can be done in 3 ways. In each case the spins can either both be up or both down. Therefore there are $3 \times 2 = 6$ orbital diagrams of equal energy. The O-atom ($Z = 8$) has an electron configuration of $1s^2 2s^2 2p^4$. The p^4 configuration requires 3 parallel spins in three separate orbitals and one additional antiparallel spin in any one of the three. There are therefore also 3 ways of doing this, each of which can have the unpaired spins either up or down. There are therefore once again six equal energy orbital diagrams.

h) For all atoms, the energies of orbitals increase with n, in the sense that the lowest n has the most negative energy, measured relative to zero for an electron that has just escaped the atom. For the H-atom the energy depends exactly on $-R_H/n^2$ where R_H is the Rydberg constant. The H-atom is also exceptional in that for a given n the energy is the same for all l values. For multi-electron atoms such as He the relationship is more complicated because of the effects of shielding of the outer electrons by inner electrons. The energy still increases with n, but cannot be expressed in a simple formula. Orbitals of a given n have lower energies than for H because of the higher charge on the He nucleus. A fundamental difference from H is that for He the energy increases with l for a given n, because the orbitals with lower l penetrate closer to the nucleus. They are therefore less shielded and feel a larger effective nuclear charge. A sketch should look something like Fig. 5.4.
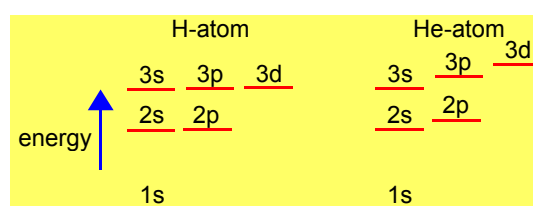

Figure 5.4: schematic H and He atomic orbital energies.

5.3   Solution

a) $n = 3$, $l = 3$, $m_l = 0$ is invalid as $n = 3$ then $l = 0, 1, 2$ *i.e.* maximum $l = (n − 1) = 2$.

b) $n = 2$, $l = 1$, $m_l = 0$ is valid it is a $2p_z$ orbital.

c) $n = 6$, $l = 5$, $m_l = −1$ is valid but does not exist, only go up to f orbitals ($l = 3$) for *ground* state atoms

d) $n = 4$, $l = 3$, $m_l = −4$ is invalid ($n = 4$, then $l = 3$ is OK) but $m_l = 0, ±1, ±2, ±3$ so $m_l = −4$ is invalid.

5.4   Solution

The yellow sodium doublet wavelengths are 588.9950 nm and 589.5924 nm note that spectroscopy can measure wavelengths to a large number of significant figures.

$$c = \lambda \nu \text{ and } E = h\nu$$
$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})(6.0220 \times 10^{23} \text{ mol}^{-1})}{588.9950 \times 10^{-9} \text{ m}} = 203.1 \text{ kJ mol}^{-1}$$
$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})(6.0220 \times 10^{23} \text{ mol}^{-1})}{589.5924 \times 10^{-9} \text{ m}} = 202.9 \text{ kJ mol}^{-1}$$
$$\Delta E = 0.2 \text{ kJ mol}^{-1}$$

Note the small difference of 0.2 kJ mol^{-1} compared with the yellow lines energies of about 200 kJ mol^{-1} or an energy difference of about 0.1%.

5.5   Solution

a) A quartet state has $2S+1 = 4$ so the total spin quantum number $S = 3/2$. The $^4D_{5/2}$ state has a total orbital angular momentum quantum number $L = 2$ and the possible values for J are given by the Clebsch-Gordon series.

$$J = L+S, \; L+S-1, \; L+S-2, \; L+S-3, \; \ldots \; |L-S|$$
$$J = 7/2 \qquad 5/2 \qquad 3/2 \qquad 1/2$$
$$^4D_{7/2} \; {}^4D_{5/2} \; {}^4D_{3/2} \; {}^4D_{1/2}$$

b) As $S = 3/2$ the minimum number of electrons that could form this state is three with their individual spins parallel to one another $S = 1/2 + 1/2 + 1/2 = 3/2$. Remember the total spin quantum number S (italic as it is variable symbol) should not be confused with S the state label (roman as it is a label).

c) This question shows that a state term symbol such as $^4D_{5/2}$ normally has several possible electron configurations of non-equivalent electrons. Conversely a particular electron configuration may leads to several different states. The only unambiguous method is to quote the both the configuration and the state together.

5.6 Solution

a) The ground electron configuration of Na is $1s^22s^22p^63s^1$.

$S = s = \frac{1}{2}$

$\text{multiplicity}(2S+1) = 2\times\frac{1}{2} + 1 = 2$ a doublet term

$L = l = 0$ an S term

$J_{max} = L+S = 0+\frac{1}{2} = \frac{1}{2}$

$J_{min} = |L-S| = |0-\frac{1}{2}| = \frac{1}{2}$

maximum = minimum, so there is only one state

$$\text{Na } 1s^22s^22p^63s^1 \ ^2S_{1/2}$$

b) The excited electron configuration of Na is $1s^22s^22p^63s^03p^1$.

$S = s = \frac{1}{2}$

$\text{multiplicity}(2S+1) = 2\times\frac{1}{2}+1 = 2$ a doublet term

$L = l = 1$ a P term

$J_{max} = L+S = 1+\frac{1}{2} = \frac{3}{2}$

$J_{min} = |L-S| = |1-\frac{1}{2}| = \frac{1}{2}$

There are two states with the same configuration Na $1s^22s^22p^63s^03p^1$

$$^2P_{3/2} \text{ and } ^2P_{1/2}$$

Hund's 3rd rule (1 p-electron out of a potential maximum of 6) gives

$$^2P_{1/2} \text{ is the lower energy excited state}$$
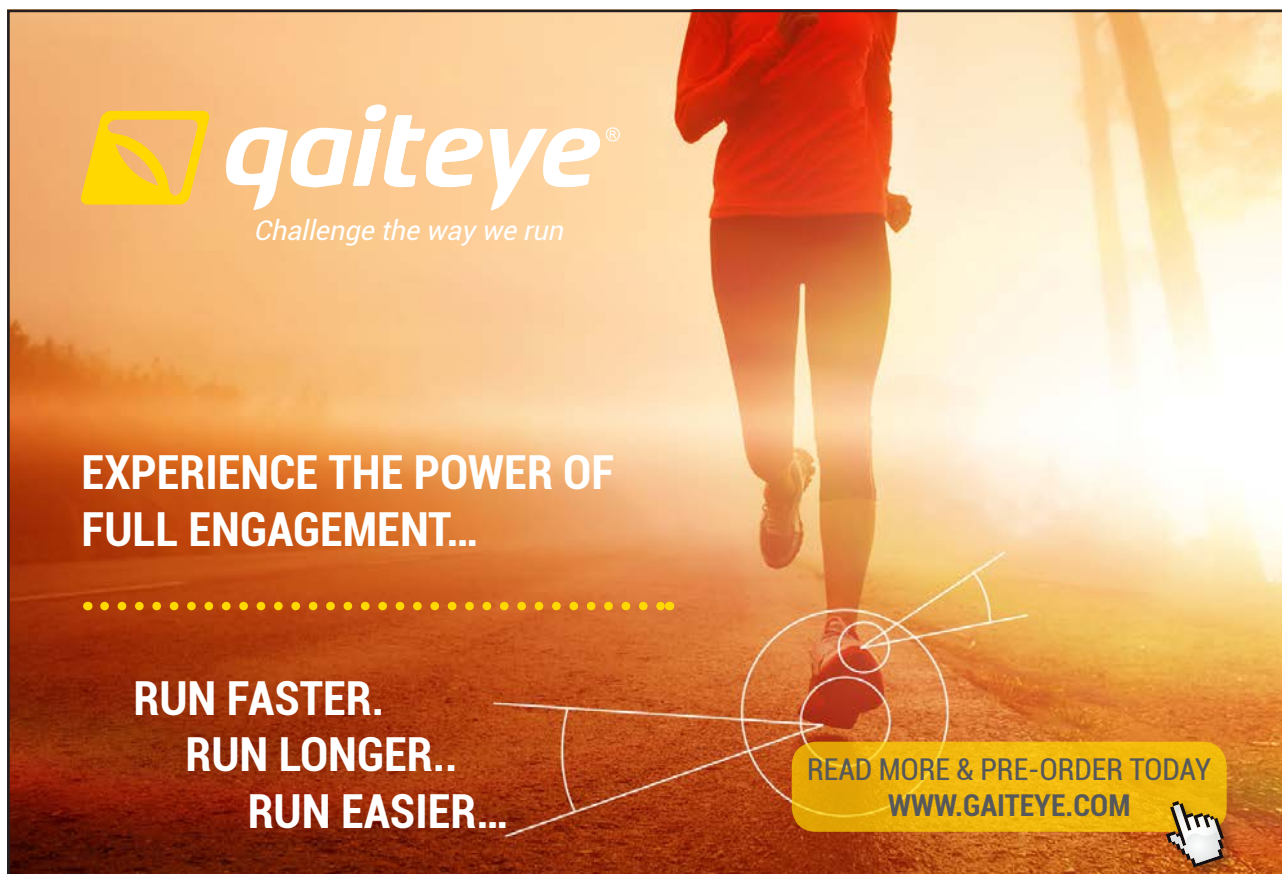
c) Russell-Saunders selection rules can be used to find the allowed and forbidden transitions between the three states, *i.e.* the ground state and the two excited states.

$$
\begin{aligned}
&(1)\ \Delta n = \text{anything}\\
&(2)\ \Delta(2S+1) = 0\\
&(3)\ \Delta L = 0, \pm 1 \text{ but } \Delta l = \pm 1\\
&(4)\ \Delta J = 0, \pm 1 \text{ but } J=0 \leftarrow\!|\!\rightarrow J=0\\
&\quad {}^{2}P_{3/2} \leftarrow\!|\!\rightarrow {}^{2}P_{1/2} \text{ because } \Delta l = 0\\
&\quad {}^{2}P_{3/2} \leftrightarrow {}^{2}S_{1/2} \text{ and } {}^{2}P_{1/2} \leftrightarrow {}^{2}S_{1/2}
\end{aligned}
$$

These are the yellow sodium doublet emissions that illuminates our streets. The excited Na atoms are obtained by collisions of sodium vapour atoms with electrons in the electric discharge plasma of the argon/neon gas filling of the "sodium" lamp.

5.7 Solution

(a) Finding the term symbols for equivalent electrons with the same values of n and l is actually more time consuming than for non-equivalent electrons. For the ground state of a C-atom with $1s^2 2s^2 2p^2$ we only have to worry about the open subshell $2p^2$ electrons. Table 5.1 shows the 15 possible ways of arranging the pair of 2p electrons, realizing that they have to obey Pauli's exclusion principle. The 15 microstates, as they are called, come from $(2S+1)(2L+1)$ which for the $2p^2$ open sub-shell has a total spin $S = 1$ and the total orbital angular momentum $L = 2$ so number microstates is $(2\times1 + 1)(2\times2 + 1)$ = 15. The list below has taken into account the interchangeability of m_{l1} and m_{l2} and also of m_{s1} and m_{s2}.

m_{l1}	m_{l2}	m_{s1}	m_{s2}	M_L	M_S	microstate	term
+1	+1	+½	−½	+2	0	(1)	^{1}D
+1	0	+½	+½	+1	+1	(2)	^{3}P
+1	0	+½	−½	+1	0	(3)	^{1}D
+1	0	−½	+½	+1	0	(4)	^{3}P
+1	0	−½	−½	+1	−1	(5)	^{3}P
+1	−1	+½	+½	0	+1	(6)	^{3}P
+1	−1	+½	−½	0	0	(7)	^{1}D
+1	−1	−½	+½	0	0	(8)	^{3}P
+1	−1	−½	−½	0	−1	(9)	^{3}P
0	0	+½	−½	0	0	(10)	^{1}S
0	−1	+½	+½	−1	+1	(11)	^{3}P
0	−1	+½	−½	−1	0	(12)	^{1}D
0	−1	−½	+½	−1	0	(13)	^{3}P
0	−1	−½	−½	−1	−1	(14)	^{3}P
−1	−1	+½	−½	−2	0	(15)	^{1}D

Table 5.1: microstates for two equivalent p electrons.

Starting with microstate (1) with the highest $M_L = +2$ which must correspond to the highest component of $L = 2$ which is a D term with electrons spins $S = 0$, $(2S+1) = 1$ a singlet, so (1) is a microstate of the ^{1}D term. As well $M_L = +2$ the full list should be $M_L = +2, +1, 0, −1, −2$ and each with $M_S = 0$ so there are five microstates of the ^{1}D term. Which microstates we choose is arbitrary, for instance (12) and (13) both have $M_L = −1$, and $M_S = 0$. The ^{1}D term's five microstates I have chosen are (1) $M_L = +2$ and $M_S = 0$; (3) $M_L = +1$ and $M_S = 0$; (7) $M_L = 0$ and $M_S = 0$; (12) $M_L = −1$, and $M_S = 0$; and the fifth (15) $M_L = −2$, and $M_S = 0$.

The microstate (2) has the next highest value of $M_L = +1$ which must correspond to the highest component of $L = 1$ which is a P term with electrons spins $S = +1$, $(2S+1) = 3$ a triplet, so (2) is a microstate of the ^{3}P term. As well $M_L = +1$ the full list should be $M_L = +1, 0, −1$, and each with $M_S = +1, 0, −1$ so there are nine microstates of the ^{3}P term. The ^{3}P term's nine microstates are (2) $M_L = +1$ and $M_S = +1$; (4) $M_L = +1$ and $M_S = 0$; (5) $M_L = +1$ and $M_S = −1$; (6) $M_L = 0$, and $M_S = +1$; (8) $M_L = 0$, and $M_S = 0$; (9) $M_L = 0$, and $M_S = −1$; (11) $M_L = −1$, and $M_S = +1$; (13) $M_L = −1$, and $M_S = 0$; and finally (14) with $M_L = −1$, and $M_S = −1$.

There is only one microstate left (10) with $M_L = 0$ and $M_S = 0$ which is the only component of the ^{1}S term.

We are almost there, except that the ^1S, ^1D and ^3P terms still need their J total angular momentum determined. For ^1S we have $S = 0$ and $L = 0$ and from the Clebsch-Gordon series we have.

$$^1S \text{ has } J = |0+0|, \ldots, |0-0| \qquad ^1S_0$$

The ^1D has $L = 2$ and $S = 0$ and so we have

$$^1D \text{ has } J = |2+0|, \ldots, |2-0| \qquad ^1D_2$$

Finally the ^3P with $L = 1$ and $S = 1$ has the following states.

$$^3P \text{ has } J = |1+1|, |1+1-1|, |1-1| \qquad ^3P_2 \ ^3P_1 \ ^3P_0$$

As the two active electrons are equivalent, they are both in the 2p subshell, Hund's rules apply to the energies of the states. From the first rule the triplet states are lower in energy than the singlet states. Hund's second rule is the $^1D < {}^1S$. Hund's third rule is that the 2p subshell is less than a half full as it could potentially hold a total of 6 and so the order is normal and the ground state is $^3P_0$. The list of electronic states for the $1s^22s^22p^2$ electron configuration is $^3P_0 < {}^3P_1 < {}^3P_2 < {}^1D_2 < {}^1S_0$.

(b) In a hydrocarbon flame or an electric discharge using graphite electrodes C-atoms can be excited by electron collision to give C-atoms with the electron configuration $1s^22s^22p^13p^1$ with two *non*-equivalent electrons in unfilled orbitals. The Pauli exclusion principle no longer applies. So $l_1 = l_2 = 1$ and $s_1 = s_2 = \frac{1}{2}$ and using the Clebsch-Gordon series we have $L = 2, 1, 0$ and $S = 1, 0$. For non-equivalent electrons we can just deal with the L, S and J values directly to find the six microstates and the ten electronic states.

L	S	J	state
2	1	3,2,1	$^3D_3 \ ^3D_2 \ ^3D_0$
2	0	2	$^1D_2$
1	1	2,1,0	$^3P_2 \ ^3P_1 \ ^3P_0$
1	0	1	$^1P_1$
0	1	1	$^3S_1$
0	0	0	$^1S_0$

Table 5.2: microstates for two non-equivalent p electrons.

These give the electronic states $^3D_3 \ ^3D_2 \ ^3D_1$ closely spaced to one another as are the $^3P_2 \ ^3P_1 \ ^3P_0$ states because they are spin-orbit split by weak magnetic forces. The 2p and 3p electrons are non-equivalent and Hund's rules no longer apply. This is shown when we look at the energy order (not asked for in the question) which is $^1P_1 < {}^3D_1 < {}^3D_2 < {}^3D_3 < {}^3S_1 < {}^3P_0 < {}^3P_1 < {}^3P_2 < {}^1D_2 < {}^1S_0$ (Kramida *et al* 2014).

6 Electronic Spectroscopy Tutorial

6.1 Question

The diatomic molecule $^1H^{127}I$ has a bond dissociation energy, $D_0 = 298$ kJ mol^{-1}. The molecule absorbs a photon with a wavelength of 253.7 nm and dissociates to the ground state ^1H and ^{127}I atoms. The momenta of the two fragments are conserved which allows you calculate the following. (a) The kinetic energies of the ^1H and ^{127}I atoms. (b) The speeds of the ^1H and ^{127}I atoms.

6.2 Question

The following data from the literature (Matsui *et al*. 2003) are the absolute term values $T(v')$ for the v' values of O_2 $B^3\Sigma_u^-$ derived from the Schumann-Runge absorption of O_2 $(B^3\Sigma_u^-\ v')\leftarrow(X^3\Sigma_g^-\ v''=0)$. Use the data to estimate the dissociation energy D_0' of O_2 in the $B^3\Sigma_u^-$ excited electronic state. In Table 6.1 the energy differences between neighbouring term values of the upper electronic state are calculated and also the average quantum number of the two neighbouring terms (the quantum number of the "gap"). Plot the energy differences between neighbours against the average quantum numbers of the neighbours and find the area under the curve to estimate D_0' using the Birge-Sponer method, see Parker (Parker 2013a, p. 19).

v'	$T(v')/\text{cm}^{-1}$	$\Delta G(V'+\frac{1}{2})/\text{cm}^{-1}$	$v'+\frac{1}{2}$
0	49356.81		
1	50044.37	687.56	0.5
2	50709.53	665.16	1.5
3	51350.78	641.25	2.5
4	51968.26	617.48	3.5
5	52559.75	591.49	4.5
6	53121.44	561.69	5.5
7	53654.72	533.28	6.5
8	54154.92	500.2	7.5
9	54621.12	466.2	8.5
10	55049.72	428.6	9.5
11	55437.75	388.03	10.5
12	55783.011	345.261	11.5
13	56083.695	300.684	12.5
14	56338.38	254.685	13.5
15	56548.168	209.788	14.5
16	56716.53	168.362	15.5
17	56848.56	132.03	16.5

Table 6.1: $T(v')$ for the O_2 $B^3\Sigma_u^-$ vibrational-electronic levels and energy gaps.

6.3 Question

The $B^3\Sigma_u^-$ excited state of O_2 dissociates to one ground state atom $O(^3P)$ and one excited state atom $O(^1D)$ at the dissociation limit. The transition $O(^1D) \leftarrow O(^3P)$ has an excitation energy of $E_{ex} = 15864.8$ cm^{-1} from atomic spectroscopy.
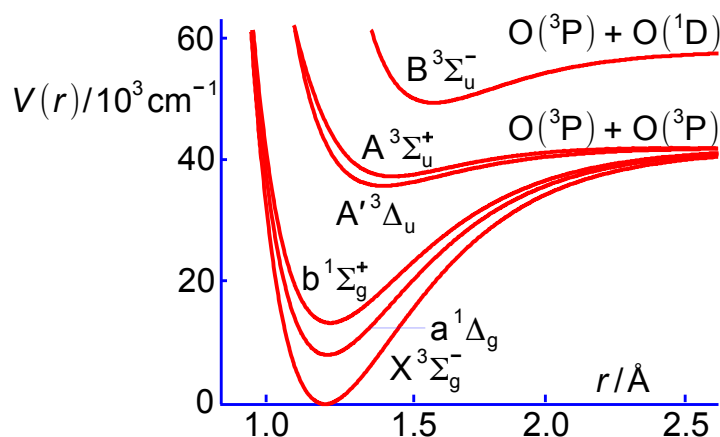
Figure 6.1: schematic PE curves of some of the electronic states of O_2.

Using the literature values (Huber and Herzberg 1979 p 490) for $D_e' = 7334.22$ cm^{-1} and $T_e' = 49793.28$ cm^{-1} for the O_2 $B^3\Sigma_u^-$ state, determine the well depth D_e'' for the ground state O_2 $X^3\Sigma_g^-$.

6.4   Question

A 2 mm path-length cell, with 0.01 mol L^{-1} solution of benzene was exposed to 256 nm light and 52% of the light was absorbed. What is (a) the absorbance and (b) the molar decadic absorption coefficient of benzene at this wavelength? Is the benzene absorption a so-called allowed or forbidden transition at this wavelength?

6.5   Question

This problem emphasizes that the two or three term anharmonic vibrational energy equation is rather poor at modelling the vibrational ladder near the dissociation limit. We will compare this simple model with the experimental spectroscopic data for C$_2$ taken from Huber and Herzberg (Huber and Herzberg 1979 p. 112) where the energies are in cm^{-1} and we use also their value for ground state bond dissociation energy of $D_0(X^1\Sigma_g) = 6.21$ eV. The C$_2$ gas-phase radical has an emission in the visible called the Swan band between two excited electronic states d$^3\Pi_g \rightarrow$ a$^3\Pi_u$ with a blue colour 340-785 nm which can be seen in hydrocarbon flames such as a blue Bunsen burner flame, comets tails and as absorption spectra in the atmosphere of stars including the Sun. Absorption spectra from an excited state is unusual, but note that T_e of the excited state a$^3\Pi_u$ is only 716.24 cm^{-1} above the T_e of the ground state X$^1\Sigma_g$. Calculate the following in wavenumbers.

a) the term values or energies of the $T(X^1\Sigma_g\ v = 0)$ and $T(a^3\Pi_u\ v = 0)$.
b) the Boltzmann thermal population ratio $n(a^3\Pi_u\ v = 0)$ to $n(X^1\Sigma_g\ v = 0)$ at 298.15 K, 500 K and 1000 K using the energy conversion factor $k_B T/hc = 207.23$ cm^{-1} at 298.15 K.

state	T_e	$\bar{v}_e$	$x_e\bar{v}_e$	$y_e\bar{v}_e$	r_e	transition	v_{00}
d$^3\Pi_g$	20022.50	1788.22	16.440	−0.5067	1.2661	d↔a Swan	19378.44
a$^3\Pi_u$	716.24	1641.35	11.67		1.31190		
X$^1\Sigma_g$	0	1854.71	13.340	−0.172	1.24253		

Table 6.2: C$_2$ data for the X$^1\Sigma_g$ and the Swan band states a$^3\Pi_u$ and d$^3\Pi_g$.

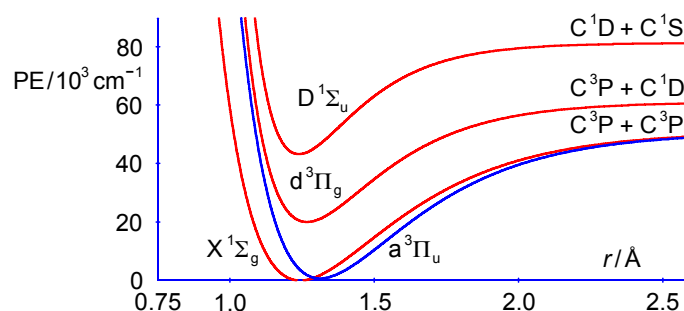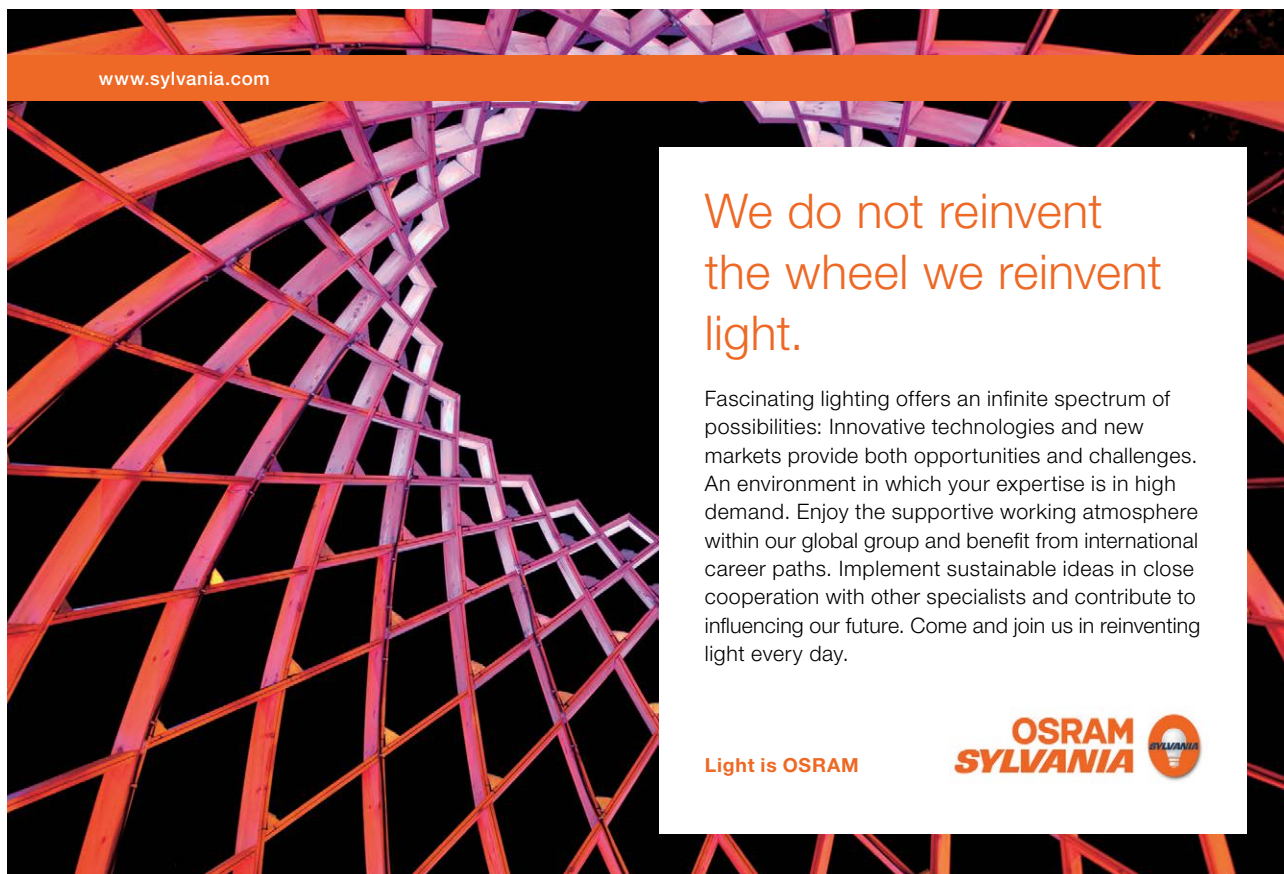**Figure 6.2:** schematic potential energy curves of some states of C$_2$.

c) Calculate the ground state dissociation $D_0(X^1\Sigma_g)$.

d) Calculate the ground state well depth $D_e(X^1\Sigma_g)$.

e) Calculate the well depth of the $a^3\Pi_u$ state knowing that $X^1\Sigma_g$ and $a^3\Pi_u$ have the same dissociation limit.

f) Calculate the dissociation energy of the lower Swan band state $D_0(a^3\Pi_u)$.

g) Calculate the term of the ground vibrational level of the upper Swan band state $T(d^3\Pi_g\ v = 0)$ knowing that the band origin of the Swan band $T(a^3\Pi_u\ v = 0) \leftrightarrow T(d^3\Pi_g\ v = 0)$ is equal to 19378.44 cm^{-1}.

h) Calculate the dissociation energy of the upper Swan band state $T(d^3\Pi_g\ v_{limit})$ using the C-atom excitation energy $C(^1D) \leftrightarrow C(^3P)$ is equal to 10192.63 cm^{-1} (Kramida *et al.* 2014).

i) Compare these exact spectroscopic experimental values with your estimate using the two-term anharmonic oscillator to estimate $D_e(X^1\Sigma_g)$.

6.1   Solution

A photon with a wavelength of 253.7 nm has an energy of

$$E = \frac{hc}{\lambda} = \frac{\left(6.626 \times 10^{-34}\,\text{J s}\right)\left(2.998 \times 10^8\,\text{m s}^{-1}\right)}{253.7 \times 10^{-9}\,\text{m}} = 7.830 \times 10^{-19}\,\text{J}$$

and a mole of such photons, or an einstein, has the energy below.

$$E = \left(7.830 \times 10^{-19}\,\text{J}\right)\left(6.022 \times 10^{23}\,\text{mol}^{-1}\right) = 471.5\,\text{kJ mol}^{-1}$$

The total kinetic energy released is $E - D_0 = (471.5\,\text{kJ mol}^{-1} - 298\,\text{kJ mol}^{-1}) = 173.5\,\text{kJ mol}^{-1}$. The fraction of kinetic energy released for the atoms is found by realizing that the momentum is conserved with the two fragments moving in opposite directions with equal and opposite momenta.

$$m_H v_H = -m_I v_I \quad \text{and so} \quad \left(m_H v_H\right)^2 = \left(m_I v_I\right)^2$$

$$\text{KE of H} \quad E_H = \frac{1}{2} m_H v_H^2 = \frac{\left(m_H v_H\right)^2}{2 m_H} \qquad \text{KE of I} \quad E_I = \frac{1}{2} m_I v_I^2 = \frac{\left(m_I v_I\right)^2}{2 m_I}$$

$$\frac{E_H}{E_H + E_I} = \frac{\left(m_H v_H\right)^2}{2 m_H} \Bigg/ \left(\frac{\left(m_H v_H\right)^2}{2 m_H} + \frac{\left(m_I v_I\right)^2}{2 m_I}\right)$$

The "2"s cancel top and bottom. Replace $(m_I v_I)^2$ by $(m_H v_H)^2$ and cancel out the $(m_H v_H)^2$ terms top and bottom.

$$\frac{E_H}{E_H + E_I} = \frac{\left(m_H v_H\right)^2}{m_H} \Bigg/ \left(\frac{\left(m_H v_H\right)^2}{m_H} + \frac{\left(m_H v_H\right)^2}{m_I}\right) = \frac{1}{m_H} \Bigg/ \left(\frac{1}{m_H} + \frac{1}{m_I}\right)$$

Bring the denominator to its own common denominator. Replace the division by a multiplication.

$$\frac{E_H}{E_H + E_I} = \frac{1}{m_H} \Bigg/ \left(\frac{1}{m_H} + \frac{1}{m_I}\right) = \frac{1}{m_H} \Bigg/ \left(\frac{m_I + m_H}{m_H m_I}\right) = \frac{1}{m_H} \times \left(\frac{m_H m_I}{m_I + m_H}\right)$$

Cancel out m_H top and bottom.

$$\frac{E_H}{E_H + E_I} = \frac{m_I}{m_I + m_H}$$

Using completely analogous algebra the KE of the I-atom is as follows.

$$\frac{E_I}{E_H + E_I} = \frac{m_H}{m_I + m_H}$$

Substituting the masses and the total KE gives us the individual KE of each of the two atoms.

$$\frac{E_H}{E_H + E_I} = \frac{126.9}{126.9 + 1.008} \times 173.5\,\text{kJ mol}^{-1} = 172.1\,\text{kJ mol}^{-1}$$

$$\frac{E_I}{E_H + E_I} = \frac{1.008}{126.9 + 1.008} \times 173.5\,\text{kJ mol}^{-1} = 1.4\,\text{kJ mol}^{-1}$$

The average kinetic energy of a gas is $3RT/2$ and at 298 K this corresponds to an average of about 3.7 kJ mol^{-1} so the KE of the H-atom of 172.1 kJ mol^{-1} has a KE equivalent to 13861 K in a bath gas of HI of 298 K. Hence the unusual reactions of these "hot" H-atom.

(b) The speed is found from the kinetic energies and the masses $m_H = 1.008 \times 1.6606 \times 10^{-27}$ kg = 1.634×10^{-27} kg and $m_I = 126.9 \times 1.6606 \times 10^{-27}$ kg = 2.1073×10^{-25} kg with the units conversion J = kg m^2 s^{-2}.

$$E = \frac{1}{2}mv^2 \quad \text{and so} \quad v = \sqrt{\frac{2E}{m}}$$

$$v_H = \sqrt{\frac{2 \times 172.1 \times 10^3\,\text{J mol}^{-1}}{(6.0220 \times 10^{23}\,\text{mol}^{-1})(1.634 \times 10^{-27}\,\text{kg})}} = 18.70\,\text{km s}^{-1}$$

$$v_I = \sqrt{\frac{2 \times 1.4 \times 10^3\,\text{J mol}^{-1}}{(6.0220 \times 10^{23}\,\text{mol}^{-1})(2.1073 \times 10^{-25}\,\text{kg})}} = 0.149\,\text{km s}^{-1}$$

So the H-atom carries away most of the kinetic energy and as a result is travelling at super-thermal speed compared with either the I-atom or the HI molecule at 298 K.

6.2   Solution

Fig. 6.3 is the plot of the energy difference between neighbouring transitions $\Delta G(v'+\frac{1}{2})$, against the average of the two neighbouring quantum numbers $(v'+\frac{1}{2})$ for the O_2 Schumann-Runge vibrational progression.
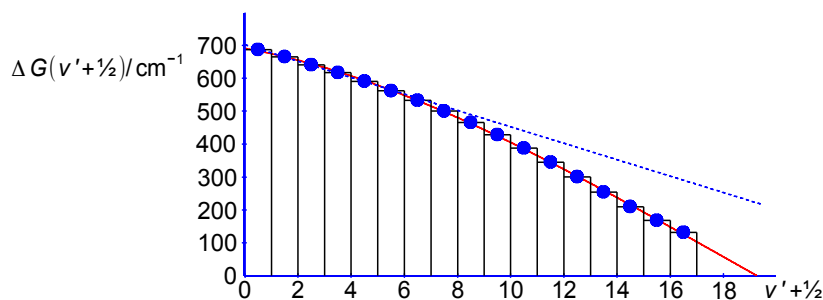
Figure 6.3: Birge-Sponer plot for the Schumann-Runge absorption of O_2.

The gap between the vibrational levels closes up due to the anharmonicity, *i.e.* it is non-linear, this is emphasized by the best straight line drawn through the first 6 data points (those most close to harmonic). Any extrapolation of a linear fit to the data points will be both inappropriate and also give much too high a value for the convergence limit. The least squares third order polynomial curve crosses the $(v'+\frac{1}{2})$ axis at $(v'+\frac{1}{2})$ = 19.2695. Measurements up to the dissociation or convergence limit are not always possible due to the relative positions of the two potential energy curves and also due to very small Franck-Condon overlap factors for transitions to high v' levels. In that situation the best use of the Birge-Sponer plot is to assume that the data points are a continuous function and not quantized which allows us to fit a polynomial to them. This "continuous" polynomial may then be integrated to find the area under the curve from $(v'+\frac{1}{2})$ = 0 to $(v'+\frac{1}{2})$ = 19.2695, *i.e.* the sum total of each energy differences. The third order anharmonic vibrational polynomial is the red line. At low values of v' a cubic polynomial may well be adequate but at high values v' the quartic and quintet terms may be progressively more important. The red line in Fig. 6.3 is the cubic polynomial shown below.

$$\Delta G\left(v'+\tfrac{1}{2}\right) = 691.27235 - 14.68204\left(v'+\tfrac{1}{2}\right) - 1.708353\left(v'+\tfrac{1}{2}\right)^2 + 0.03151806\left(v'+\tfrac{1}{2}\right)^3 \ \mathrm{cm}^{-1}$$

$$D_0' = \int_0^{19.2695} 691.27235 - 14.68204\,(v'+\tfrac{1}{2}) - 1.708353\,(v'+\tfrac{1}{2})^2 + 0.03151806\,(v'+\tfrac{1}{2})^3 \; \mathrm{d}\,(v'+\tfrac{1}{2}) \; \mathrm{cm}^{-1}$$

$$D_0' = \left[691.27235\,(v'+\tfrac{1}{2}) - \frac{14.68204}{2}(v'+\tfrac{1}{2})^2 - \frac{1.708353}{3}(v'+\tfrac{1}{2})^3 + \frac{0.03151806}{4}(v'+\tfrac{1}{2})^4 \right]_0^{19.2695} \mathrm{cm}^{-1}$$

$$D_0' = 7606.59268 \; \mathrm{cm}^{-1}$$

Note that the integration has been carried out with an an excessive number of significant figures to reduce any rounding errors. But how accurate, let alone how precise, is this result compared with the "true" value? In the case of O_2 we can compare this extrapolation with the experimentally measured convergence limit for the Schumann-Runge band which has been measured directly by spectroscopy. The literature values from the NIST Chemistry web book (NIST 2014) for the well depth and dissociation energy of the $B^3\Sigma_u^-$ state are $D_e' = 7334.22$ cm^{-1} and $D_0' = 6982.24$ cm^{-1}. The Birge-Sponer extrapolation method of treating the function as a continuous variable and integrating over-estimates the excited state dissociation energy by 9%. The question shows that the treatment of experimental data may not be straight forward and should be viewed with care particularly where data handling involves an extrapolation of the data.

6.3   Solution

Energetically we have

$$T_e' + D_e' = D_e'' + E_{ex} \qquad 49793.28 \, \mathrm{cm}^{-1} + 7334.22 \, \mathrm{cm}^{-1} = D_e'' + 15864.8 \, \mathrm{cm}^{-1}$$

$$D_e'' = 41262.7 \, \mathrm{cm}^{-1}$$

The $X^3\Sigma_g^-$ O_2 ground state has a much stronger bond (41262.7 cm^{-1}) than the $B^3\Sigma_u^-$ state (7334.22 cm^{-1}) which is reflected in their equilibrium bond lengths $r_e(X^3\Sigma_g^-) = 1.2075$ and $r_e(B^3\Sigma_u^-) = 1.6042$ Å.

6.4   Solution

From the Beer-Lambert law we can calculate the molar absorption coefficient.

$$A = \log\frac{I_0}{I} = \varepsilon\,c\,l \qquad \log\frac{100}{48} = \varepsilon\,(0.01 \; \mathrm{mol \; L}^{-1})(0.2 \; \mathrm{cm})$$
$$\varepsilon = 159.4 \; \mathrm{L \; mol}^{-1} \; \mathrm{cm}^{-1}$$

The absorption is a "forbidden" process, or possibly not very near the maximum for an allowed absorption, as typical values of absorption coefficients for allowed transitions near to λ_{max} are $\varepsilon \approx 10^3\text{-}10^5$ L mol^{-1} cm^{-1}.

6.5   Solution

The C_2 Swan band states are summarized below along with the ground state data.

state	T_e	$\bar{v}_e$	$x_e\bar{v}_e$	$y_e\bar{v}_e$	r_e	transition	v_{00}
d$^3\Pi_g$	20022.50	1788.22	16.440	−0.5067	1.2661	d↔a Swan	19378.44
a$^3\Pi_u$	716.24	1641.35	11.67		1.31190		
X$^1\Sigma_g$	0	1854.71	13.340	−0.172	1.24253		

a) The term values (energies) for $T(X^1\Sigma_g \ v = 0)$ and $T(a^3\Pi_u \ v = 0)$ are calculated below.

$$T(X, v=0) = 0 + \left(\tfrac{1}{2}\times 1854.71\right) - \left(\tfrac{1}{4}\times 13.34\right) - \left(\tfrac{1}{8}\times 0.172\right) = 924.00 \text{ cm}^{-1}$$
$$T(a, v=0) = 716.24 + \left(\tfrac{1}{2}\times 1641.35\right) - \left(\tfrac{1}{4}\times 11.67\right) = 1534.00 \text{ cm}^{-1}$$

b) The Boltzmann thermal population ratio $n(a^3\Pi_u \ v = 0)$ to $n(X^1\Sigma_g \ v = 0)$ is calculated as below.

$$\frac{n(a, v=0)}{n(T, v=0)} = \exp-\frac{T(a, v=0)-T(X, v=0)}{k_B T/hc}$$
$$\frac{n(a, v=0)}{n(T, v=0)} = \exp-\frac{1534.00 - 924.00 \text{ cm}^{-1}}{207.23 \text{ cm}^{-1}} = 0.05268 = 5.28\% \text{ at } 298.15 \text{ K}$$
$$\frac{n(a, v=0)}{n(T, v=0)} = \exp-\frac{1534.00 - 924.00 \text{ cm}^{-1}}{347.53 \text{ cm}^{-1}} = 0.1729 = 17.29\% \text{ at } 500 \text{ K}$$
$$\frac{n(a, v=0)}{n(T, v=0)} = \exp-\frac{1534.00 - 924.00 \text{ cm}^{-1}}{695.05 \text{ cm}^{-1}} = 0.4158 = 41.58\% \text{ at } 1000 \text{ K}$$

Even at room temperature about 5% of the C_2 is in the a$^3\Pi_u$ state giving a strong absorption spectrum.

c) From the experimental dissociation energy of 6.21 eV we have the ground state dissociation $D_0(X^1\Sigma_g)$.

$$D_0(X^1\Sigma_g) = 6.21 \text{ eV}\times 8065.5 \text{ cm}^{-1}/\text{eV} = 50086.76 \text{ cm}^{-1}$$

d) We have already calculated the $G(X^1\Sigma_g \ v = 0)$ in part (a) as 924.00 cm^{-1} this allows us to find the ground state well depth $D_e(X^1\Sigma_g)$ using the $D_0(X^1\Sigma_g) = 50086.76$ cm^{-1} value from part (c).

$$D_e(X^1\Sigma_g) = D_0(X^1\Sigma_g) + G(X^1\Sigma_g v=0) = 50086.76 + 924.00 = 51010.76 \text{ cm}^{-1}$$

e) We can calculate the well depth of the $a^3\Pi_u$ state using the fact that $X^1\Sigma_g$ and $a^3\Pi_u$ have the same dissociation limit.

$$T\left(a^3\Pi_u\, v_{limit}\right) = D_e\left(X^1\Sigma_g\right) = 51010.76 \text{ cm}^{-1}$$
$$D_e\left(a^3\Pi_u\right) = T\left(a^3\Pi_u\, v_{limit}\right) - T_e\left(a^3\Pi_u\right) = 51010.76 - 716.24 = 50294.52 \text{ cm}^{-1}$$

f) We can calculate the dissociation energy of the lower Swan band state $D_0(a^3\Pi_u)$ as we know the terms for both its limit and its ground vibrational level.

$$D_0\left(a^3\Pi_u\right) = T\left(a^3\Pi_u\, v_{limit}\right) - T\left(a^3\Pi_u\, v=0\right) = 51010.76 - 1534.00 = 49476.76 \text{ cm}^{-1}$$

g) We can calculate the term of the ground vibrational level of the upper Swan band state $T(d^3\Pi_g\ v = 0)$ using the band origin of the Swan band $T(a^3\Pi_u\ v = 0) \leftrightarrow T(d^3\Pi_g\ v = 0) = 19378.44$ cm^{-1}.

$$T\left(d^3\Pi_g\, v=0\right) = T\left(a^3\Pi_u\, v=0\right) + \left(T\left(a^3\Pi_u\, v=0\right) \leftrightarrow T\left(d^3\Pi_g\, v=0\right)\right)$$
$$T\left(d^3\Pi_g\, v=0\right) = 1534.00 + 19378.44 = 20912.44 \text{ cm}^{-1}$$

h) Using the C-atom excitation energy C(^{1}D) $\leftrightarrow$ C(^{3}P) = 10192.63 cm^{-1} we can calculate the dissociation energy of the upper Swan band state $T(\mathrm{d}^3\Pi_\mathrm{g}\, v_\mathrm{limit})$.

$$T\left(\mathrm{d}^3\Pi_\mathrm{g}\, v_\mathrm{limit}\right) = T\left(\mathrm{a}^3\Pi_\mathrm{u}\, v_\mathrm{limit}\right) + C\left(^1D\right) \leftrightarrow C\left(^3P\right)$$
$$T\left(\mathrm{d}^3\Pi_\mathrm{g}\, v_\mathrm{limit}\right) = 51010.76 + 10192.63 = 61203.39 \text{ cm}^{-1}$$

We have from the literature, the term for the upper state of the Swan band $T_\mathrm{e}(\mathrm{d}^3\Pi_\mathrm{g})$ = 20022.50 cm^{-1} so we can calculate the D_e and D_0 for this excited state.

$$D_\mathrm{e}\left(\mathrm{d}^3\Pi_\mathrm{g}\right) = T\left(\mathrm{d}^3\Pi_\mathrm{g}\, v_\mathrm{limit}\right) - T_\mathrm{e}\left(\mathrm{d}^3\Pi_\mathrm{g}\right)$$
$$D_\mathrm{e}\left(\mathrm{d}^3\Pi_\mathrm{g}\right) = 61203.39 - 20022.50 = 41180.89 \text{ cm}^{-1}$$

$$D_0\left(\mathrm{d}^3\Pi_\mathrm{g}\right) = T\left(\mathrm{d}^3\Pi_\mathrm{g}\, v_\mathrm{limit}\right) - T_\mathrm{e}\left(\mathrm{d}^3\Pi_\mathrm{g}\, v=0\right)$$
$$D_0\left(\mathrm{d}^3\Pi_\mathrm{g}\right) = 61203.39 - 20918.44 = 40284.95 \text{ cm}^{-1}$$

(i) We can estimate $D_\mathrm{e}(\mathrm{X}^1\Sigma_\mathrm{g})$ from the anharmonicity constant calculated from the literature values.

$$x_\mathrm{e}\left(\mathrm{X}^1\Sigma_\mathrm{g}\right) = \frac{x_\mathrm{e}\bar{v}_\mathrm{e}}{\bar{v}_\mathrm{e}} = \frac{13.34\,\text{cm}^{-1}}{1854.71\,\text{cm}^{-1}} = 7.1925\times10^{-3}$$

The two-terms of the anharmonic oscillator give an estimate of the convergence limit.

$$G(v) = \left(v+\tfrac{1}{2}\right)\bar{v}_\mathrm{e} - \left(v+\tfrac{1}{2}\right)^2 x_\mathrm{e}\bar{v}_\mathrm{e} \qquad G(v+1) = \left(v+\tfrac{3}{2}\right)\bar{v}_\mathrm{e} - \left(v+\tfrac{3}{2}\right)^2 x_\mathrm{e}\bar{v}_\mathrm{e}$$
$$\Delta G(v+1,v) = \bar{v}_\mathrm{e} - 2(v+1)x_\mathrm{e}\bar{v}_\mathrm{e} \text{ and at the limit } \Delta G(v+1,v)\to 0$$
$$v_\mathrm{limit} = \frac{1}{2\,x_\mathrm{e}} - 1$$

The limit must be an integer.

$$v_\mathrm{limit} = \frac{1}{2\times 7.1925\times10^{-3}} - 1 = 68.52 \approx 68\,\text{or}\,69$$

We can now estimate $T(\mathrm{X}^1\Sigma_\mathrm{g}\, v_\mathrm{limit})$ using the two term anharmonic oscillator function.

$$G(v) = \left(v+\tfrac{1}{2}\right)\bar{v}_\mathrm{e} - \left(v+\tfrac{1}{2}\right)^2 x_\mathrm{e}\bar{v}_\mathrm{e}$$
$$T\left(\mathrm{X}^1\Sigma_\mathrm{g}\, v_\mathrm{limit}\right) = 68.5\times1854.71 - 68.5^2\times13.34 = 64453.02\,\text{cm}^{-1}$$

As $T_e(\mathrm{X}^1\Sigma_g) = 0$ cm^{-1} the well depth estimated by the two-term anharmonic equation is below.

$$D_e(\mathrm{X}\,^1\Sigma_g) = 64453.02\,\mathrm{cm}^{-1}$$

The experimental spectroscopic value calculated in (d) is 51010.76 cm^{-1} for the ground state well depth. Note that the use of the two-term anharmonic oscillator function grossly overestimates the well depth D_e and the bond dissociation energy D_0 as compared with the experimental value. The quadratic anharmonicity equation is only a reasonable approximation near the bottom of the PE well and is inadequate near the dissociation limit where the cubic, quartic and quintic polynomial anharmonic vibrational terms are also required.

We have now covered some of the questions which are typical of a workshop or tutorial assignment. Tutorial and workshop questions are designed to stretch you and are not practice exam questions. Remember that exam questions are normally much shorter and are written to be solved with just a calculator as computers are generally not allowed in exams. Hopefully this book along with the textbook *Chemistry: Quantum Mechanics and Spectroscopy* (Parker 2015) will help you with quantum mechanics and spectroscopy in your chemistry based degree. Help is also available for the Maths required for your degree (Parker 2013b, 2012 and 2013a). Good luck with your studies!

7 References

Huber, KP & Herzberg, G 1979, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold Company, New York.

Kramida, A Ralchenko, Yu Reader, J & NIST ASD Team (2014), *NIST Atomic Spectra Database (ver. 5.2)*, http://physics.nist.gov/asd accessed 2014 December 20, National Institute of Standards and Technology, Gaithersburg, MD.

Matsui,T Cheung, AS-C Leung, KW-S Yoshino, K Parkinson, WH Thorne, AP Murray, JE Ito, K & Imajo, T 2003, *Journal of Molecular Spectroscopy*, vol. 219, p. 45–57.

Parker, JE 2015, *Chemistry: Quantum Mechanics and Spectroscopy*, bookboon.com, Copenhagen.

Parker, JE 2013b, *Introductory Maths for Chemists: Chemistry Maths 1*, 2nd edn. bookboon.com, Copenhagen.

Parker, JE 2012, *Intermediate Maths for Chemists: Chemistry Maths 2*, bookboon.com, Copenhagen.

Parker, JE 2013a, *Advanced Maths for Chemists: Chemistry Maths 3*, bookboon.com, Copenhagen.